Carbon (δ^{13}C) and Strontium (^{87}Sr/^{86}Sr)- based chemostratigraphy of the Oxfordian series in the Lower Saxony Basin of Northern Germany

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Abstract

The Late Jurassic (ca. 161.5-145 Ma) witnessed significant changes in climate, sea-level, and global sedimentation patterns due to the break-up of the supercontinent Pangea. During this time, the Oxfordian interval in particular experienced multiple and pronounced perturbations of the global carbon cycle. To better understand these changes, shoal-water carbonate rocks, which archive important signatures of the biosphere's evolution, can be studied.

The Lower Saxony Basin (LSB) was located in the Boreal Realm during the Late Jurassic and was characterized by widespread shallow-marine carbonate deposition. Despite multiple biostratigraphic schemes that have been developed, the stratigraphy and subdivision of the Upper Jurassic rocks of the LSB are still poorly defined. Due to the scarcity of reliable biostratigraphic markers and numerous sedimentary gaps, the stratigraphic age assignment is still uncertain and hampers further studies on a basin-wide scale.

In order to reconstruct stratigraphic correlation and paleoclimatic interpretation, three well-accessible sections (Bisperode section, Osterwald section, Langenberg section) and a scientific borehole (Konrad #101 core) were studied within the LSB. A high-resolution carbonate microfacies and sequence stratigraphy are first analyzed, which forms the baseline for the conceptualization of a reef-bearing carbonate ramp model. The supra-regional correlation of the observed sequences is discussed.

Chemostratigraphy represents a reliable technique correlation and calibration of biostratigraphic schemes on local and global scales. However, new biocalcite-derived $^{87}Sr/^{86}Sr$ results from the Oxfordian Korallenoolith Formation in LSB fail to provide an improved age assignment, possibly due to environmental factors such as continental freshwater discharge affecting the seawater $^{87}Sr/^{86}Sr$ ratios recorded in the studied shell material. In addition, a high-resolution carbonate $\delta^{13}C_{carb}$ record is presented and compared with other existing records collected from the LSB as well as from Tethyan and proto-Atlantic sites. The $\delta^{13}C_{carb}$ data enable the refinement of the pre-existing biostratigraphic framework and the establishment of a high-resolution carbon isotope-based correlation scheme. The new framework improves the stratigraphic correlation between the western and eastern parts of the LSB and allows for a better assessment of the impact of carbon cycle disturbances on the shallow-marine carbonate systems in this area. The study provides critical insights into the global pacing of the Oxfordian carbon isotope excursions and the role of environmental factors in shaping them.

Keywords: Oxfordian; shallow-marine carbonate deposits; Lower Saxony Basin; sequence stratigraphy; chemostratigraphy

Kurzfassung

Die späte Jurazeit (ca. 161.5-145 Ma) war Zeuge bedeutender globaler Veränderungen des Klimas, des Meeresspiegels und der marinen Sedimentationsmuster infolge des Auseinanderbrechens des Superkontinents Pangäa. Während dieser Zeit kam es insbesondere im Oxfordium zu zahlreichen Störungen des globalen Kohlenstoffkreislaufs. Um diese Veränderungen besser zu verstehen, können Karbonatgesteine, die wichtige Archive der Entwicklung der Biosphäre darstellen, untersucht werden.

Das Niedersächsische Becken (NB) befand sich während des späten Jura im borealen Bereich und war durch kontinuierliche flachmarine Karbonatablagerung gekennzeichnet. Trotz mehrerer biostratigraphischer Zonierungen, die erstellt wurden, sind die Stratigraphie und Unterteilung der Gesteine des oberen Jura im NB immer noch schlecht definiert. Aufgrund des Mangels an biostratigraphischen Markern und zahlreicher Hiaten ist die stratigraphische Datierung nach wie vor unsicher und erschwert weitere Studien im gesamten Becken. Um die stratigraphische Korrelation und die paläoklimatische Interpretation zu rekonstruieren, wurden drei sedimentäre Abfolgen in Aufschlüssen (Bisperode, Osterwald, Langenberg) und eine wissenschaftliche Bohrung (Konrad-Kern #101) untersucht. Zunächst wurden eine hochauflösende Karbonat-Mikrofazies Analyse und eine sequenzstratigraphische Analyse durchgeführt, welche die Grundlage für die Konzeption eines riff-führenden Karbonat-Rampenmodells bilden. Die überregionale Korrelation der beobachteten Sequenzen wurde anschließend diskutiert.

Die Chemostratigraphie stellt ein zuverlässiges Mittel dar, biostratigraphische Schemata auf lokaler und globaler Ebene zu vergleichen und zu kalibrieren. Neue, aus Biocalcit gewonnene $^{87}Sr/^{86}Sr$-Daten der Korallenoolith-Formation (Oxfordium) im NB konnten jedoch keine genaue Alterszuordnung liefern, was möglicherweise auf Umweltfaktoren wie kontinentalen Süßwassereintrag zurückzuführen ist, welche die aus Schalenmaterial abgeleiteten $^{87}Sr/^{86}Sr$-Verhältnisse im Meerwasser beeinflussen. Um diese Einschränkungen zu beheben, wird eine hochauflösende C-Isotopen ($\delta^{13}C_{carb}$) Kurve präsentiert und mit anderen bestehenden Aufzeichnungen aus der Tethys und dem Proto-Atlantik verglichen. Die $\delta^{13}C$-Daten ermöglichen die Verfeinerung des bereits bestehenden biostratigraphischen Rahmens und die Erstellung eines hochauflösenden stratigraphischen $\delta^{13}C_{carb}$-Korrelationsdatensatzes. Der neue Rahmen verbessert die Korrelationsfähigkeit zwischen den westlichen und östlichen Teilen des NB und ermöglicht eine bessere Einschätzung der Auswirkungen von Störungen des Kohlenstoffkreislaufs auf die flachmarinen Karbonatsysteme im NB. Diese Studie liefert kritische Einblicke in das globale Tempo der Kohlenstoffisotopenexkursionen im Oxfordium und die Rolle von Umweltfaktoren bei ihrer Gestaltung.

Schlüsselwörter: Oxfordium; Flachmarine Karbonatablagerungen; Niedersächsisches Becken; Sequenzstratigraphie; Chemostratigraphie

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1. Introduction

Carbonate rocks hold the potential to preserve biological, chemical, or physical signatures of biosphere's evolution through time (Weissert 2000). Deep-time shallow-marine carbonates represent highly sensitive ecological systems and can provide powerful evidence to our understanding of the climate system, sea-level change, and response mechanisms of the biosphere to pCO$_2$ perturbations (Immenhauser et al. 2008; Huck and Heimhofer 2015; Lear et al. 2020). In the near future, large-scale changes of the global carbon cycle are predicted to continue (Lear et al. 2020), and studying the geologic past might offer some critical insights into potential consequences and solutions associated with anthropogenic pCO$_2$ increase. Research efforts to understand the long-term history of the global carbon cycle based on its carbon isotopic signature have been ongoing for many decades (Jeltsch-Thömmes and Joos 2020). For instance, the Late Jurassic corresponds to a unique time interval characterized by multiple perturbations of the global carbon cycle (Padden et al. 2001, 2002; Weissert and Erba 2004). During the Late Jurassic, the Oxfordian is a key period, for which the sedimentary record indicates significant changes in global climate and sea level (e.g. Hallam 2001; Dromart et al. 2003; Cecca et al. 2001; Collin et al. 2005; Louis-Schmid et al. 2007a, 2007b; Ramajo and Aurell 2008; Boulila et al. 2010).

1.1 Late Jurassic paleogeography and sea-level changes

The Jurassic Period (ca. 201–144 Ma) constitutes the middle period of the Mesozoic Era and is named after the Jura Mountains in Switzerland, where limestone strata from this interval were first described (Gradstein et al. 2020). The Jurassic is subdivided into 11 stages based on ammonite biostratigraphy (Gradstein et al. 2020) and complemented by chemo-, magneto-, and cyclostratigraphy as well as by other biostratigraphic indicators (e.g., calcareous nannofossils). This time period is marked by fundamental reorganizations of paleogeography, paleoceanography, and ecosystems (Ziegler 1990). During the Late Jurassic, the break-up of the supercontinent Pangea continued with different spreading centers and oceanic rifts forming between North America, Eurasia, and Gondwana, and between the various segments of Gondwana itself (Ziegler 1990; Weissert and Mohr 1996; Padden et al. 2001, 2002; Hesselbo et al. 2020) (Fig. 1). This created more coastlines and shallow seas and shifted the climatic conditions from the continental dry Triassic climate towards more humid conditions prevailing during the Jurassic, indicated in the sedimentary record by the replacement of many arid areas into lush forests (Frakes et al. 1992).

In western Europe, Jurassic strata are well exposed with extensive and shallow-marine carbonate deposits and abundantly accessible outcrops. Good examples include the Jurassic Coast World Heritage Site in the UK, or the outcrops of Solnhofen, Langenberg, and Bisperode in Germany, where well exposed marine sequences indicate a time when much of the Central European continent was submerged under shallow tropical seas.
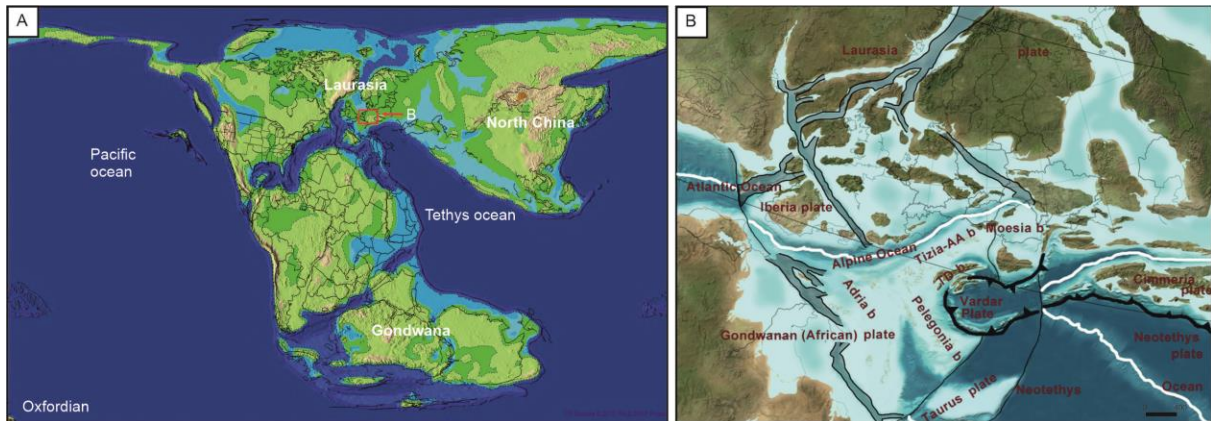
Fig.1 - A) Paleogeographic map for the Late Jurassic (Oxfordian) (<u>PaleoDEM Resource – Scotese and Wright (2018) – EarthByte</u>). B) Enlargement of the area defined by the red box in (A) with the study area labeled with a red asterisk. (Map adapted from Jon Blakey, NAU Geology https://www2.nau.edu/rcb7/).

The Late Jurassic sea-level evolution was marked by a gradual rise, modulated by third-order sea-level changes. The maximum of the second-order transgressive trend was reached during the Late Kimmeridgian–Early Tithonian transition (Ponsot and Vail 1991; Hardenbol et al. 1998; Haq 2018). Climatic conditions paralleled sea-level evolution and are generally considered as an overall warm and equable climate with high atmospheric pCO_2 levels, punctuated by few cold snap episodes (Weissert and Mohr 1996; Dromart et al. 2003; Louis-Schmid et al. 2007a, 2007b; Sellwood et al. 2008) (Fig. 2). These relatively warm conditions are reflected in the development and wide distribution of shallow-marine carbonate platforms, ramps, and barrier reefs (Leinfelder et al. 2002; Dromart et al. 2003).
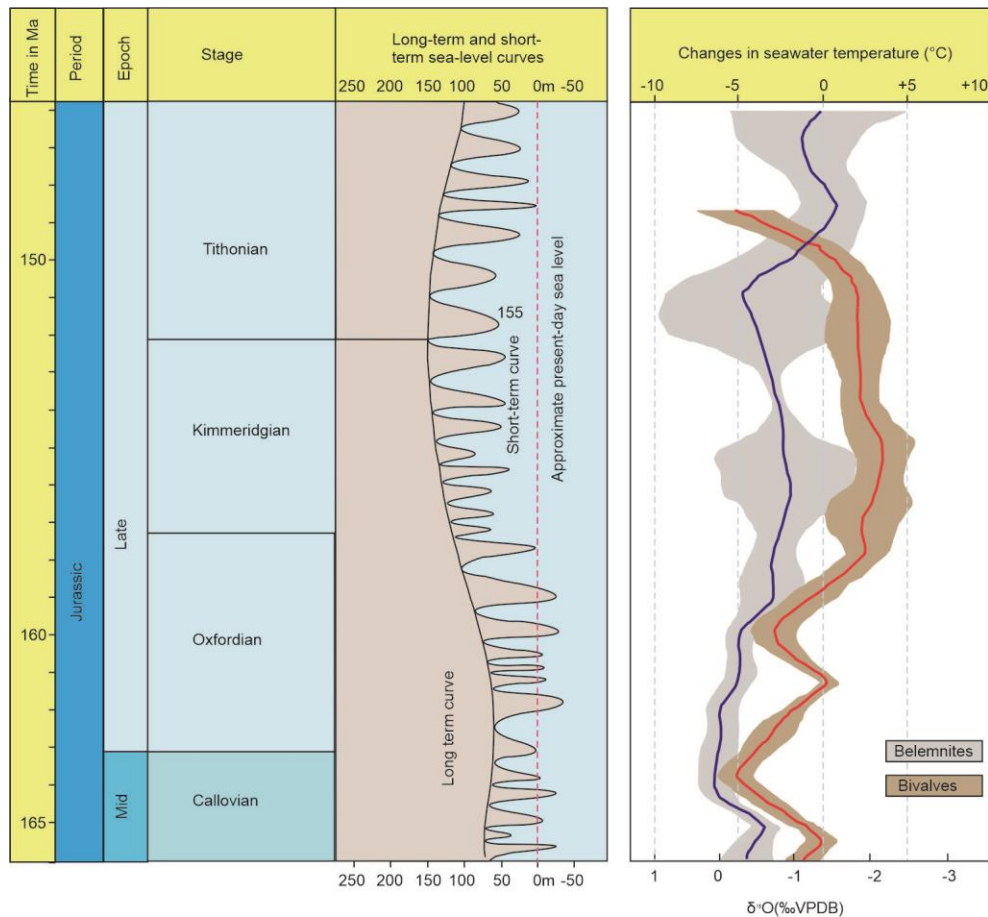
Fig. 2 - Global eustatic sea-level trend and marine paleotemperatures inferred from different types of shell material for the Late Jurassic (after Dera et al. 2011 and Haq 2018).

1.2 Chemostratigraphy

1.2.1 Carbon isotope

Carbon isotope ($\delta^{13}C_{carb/org}$) stratigraphy is central to our understanding of the connections within the ocean-atmosphere-biosphere system (Cramer and Jarvis 2020) and has been verified as a reliable way of contrasting and calibrating biostratigraphic schemes on local and global scales (Weissert 1989; Jenkyns et al. 2002; Huck et al. 2013; Frijia et al. 2015) (Fig. 3). Due to the potential of diagenetic alteration, using $\delta^{13}C$ bulk signatures for stratigraphic purposes can be problematic in shallow-water carbonates (Immenhauser et al., 2008). Generally, the pelagic bulk carbonate record stores valuable information allowing for reconstruction and a better understanding of disturbances of the exogenic carbon cycle (e.g. Scholle and Arthur 1980; Weissert 1989). However, more recent research showed that neritic carbonates can preserve a global marine $\delta^{13}C$ signature (e.g. Huck et al. 2011; Huck and Heimhofer 2015; Huck et al. 2017; Zuo et al. 2018).
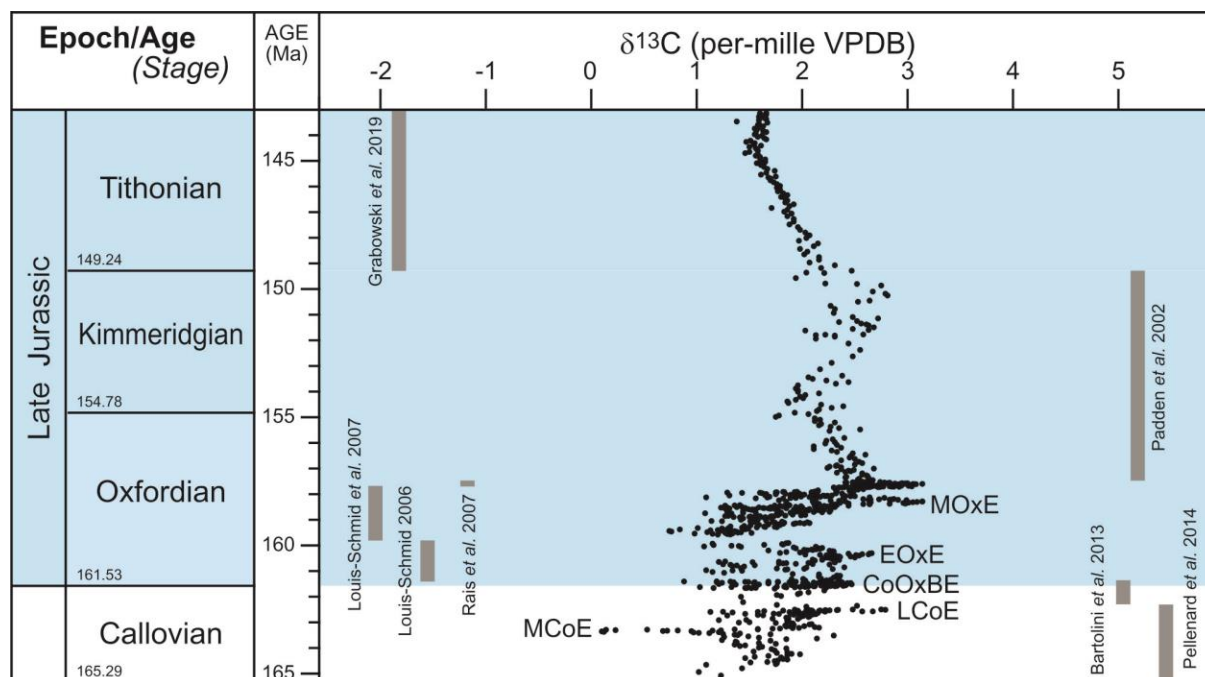
Fig. 3 - Late Jurassic composite δ¹³C stratigraphy (adopted from Cramer and Jarvis, 2020).

Carbon isotope studies of Upper Jurassic strata have been carried out in both, pelagic and shallow-marine or neritic depositional environments in the Tethyan domain (e.g. Weissert and Mohr 1996; Cecca et al. 2001; Padden et al. 2002; Rais et al. 2007; Louis-Schmid et al. 2007b, 2007a; Coimbra et al. 2009; O'Dogherty et al. 2018; Eltom et al. 2018; Carmeille et al. 2020). Across this time interval, multiple δ¹³C perturbations have been identified, incl. a pronounced positive δ¹³C shift (~1.5‰ to 4‰), termed the Middle Oxfordian Event (MOxE; Cramer and Jarvis 2020). However, with a few notable exceptions, most of these records are from the Tethyan domain (Cramer and Jarvis 2020; Eldrett 2022) and consist of relatively low-resolution datasets, which hampers precise correlations among different sections from other parts of the world. In order to better understand the response of carbonate producers to changing oceanographic and climate conditions during the Upper Jurassic, additional records need to be studied from more widespread geographic regions (Eldrett 2022). During the Late Jurassic, the Lower Saxony Basin (LSB) was located in the Boreal Realm and characterized by extensive shallow-marine carbonate deposition (Gramann et al. 1997). Hence, stratigraphic records from the LSB will enable a high-resolution investigation of the δ¹³C trend, which will help to explore and re-evaluate the nature and origin of the Late Jurassic carbon isotope perturbations.

1.2.2 Strontium isotopes

Secular variations of the strontium isotope ratio ($^{87}Sr/^{86}Sr$) are widely used as a stratigraphic tool known as strontium isotope stratigraphy (SIS), which is important for correlation and dating of sedimentary sequences to obtain reliable geochronological information (Jones 1994; McArthur et al., 2001, 2012, 2020; Jenkyns et al., 2002, Huck et al., 2013; Frijia et al., 2015; Kuznetsov et al. 2018). For the Jurassic Period, belemnite and oyster data have been faithfully used as a substrate, which is considered to preserve the contemporaneous seawater strontium isotope ratios (Jones 1992; Jones et al. 1994;

Schneider et al. 2009; Wierzbowski et al., 2017). Based on the available datasets, the Jurassic strontium isotope curve has already been documented in considerable detail (Fig. 4). Most SIS studies with a focus on the Oxfordian have been carried out on pelagic deposits, whereas analyses from shallow-water carbonates are comparatively rare. Up to now, only a limited amount of SIS data is available for the Oxfordian (Jones 1992; Jones et al. 1994; McArthur et al. 2012; Wierzbowski et al. 2017). Within the LSB, Zuo et al. (2018) used SIS to successfully refine the Kimmeridgian stratigraphic framework. Although Bruhn et al. (2005) presented a limited number of ^{87}Sr/^{86}Sr ratios from bulk carbonate samples for the Oxfordian, a more precise dating and correlation for the Oxfordian within the LSB is still lacking. In this thesis, new data from the LSB (incl. material from the Bisperode section and Konrad #101 core) will be compared with the previously published ^{87}Sr/^{86}Sr records.
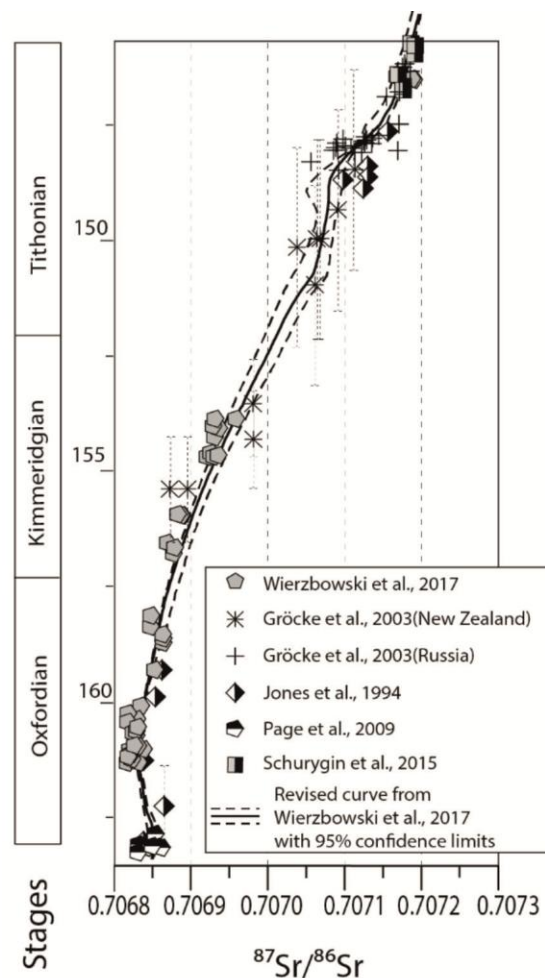
Fig. 4 - Strontium isotope trend of the Late Jurassic after Wierzbowski et al. (2017).

1.3 Geological setting

During the Late Jurassic, the Central European Basin System (CEBS) experienced extensional movements and moderate subsidence, induced by the crustal bulging of the 'North Sea Rift Dome' (Ziegler 1990). This instability resulted in extensive syn-sedimentary faulting in the CEBS with high subsidence in some areas and crustal uplifts in others (Betz et al. 1987). The LSB is located on the southern margin of the CEBS and represents one of several rifts- and wrench-induced "marginal

troughs'', that formed a series of E-W trending horst-and-graben structures (Betz et al. 1987; Ziegler 1990; Senglaub et al. 2006). The LSB has a length of ~300 km and a width of ~65 km and is bordered by the Rhenish Massif to the south and the Ringkøbing-Fyn High to the north. The sedimentary pile included within the LSB is estimated at ~4000 m in thickness (Betz et al. 1987; Mazur et al. 2005; Kästner et al. 2010) (Fig.1). It represents the most important oil and gas province in Germany and one of the oldest oil-producing basins in the world (Boigk 1981; Binot et al. 1993). The evolution of the LSB began during the Permian with extensional movements and moderate subsidence, which reached its maximum in Late Jurassic to Early Cretaceous times (Betz et al. 1987; Kneuker et al. 2020). During the Late Cretaceous, a major inversion phase affected the entire LSB, which caused uplift and erosion of large parts of the sedimentary succession deposited during the Early and early Late Cretaceous (Senglaub et al. 2006). Uplift/erosion was most pronounced in the basin center and decreased towards the north (Petmecky et al. 1999). During the Early Cenozoic, sedimentation was reestablished, and marine shales and other deposits accumulated, which now unconformably overlie the deformed Cretaceous and Jurassic strata (Kneuker et al. 2020).

1.3.1 Oxfordian strata in the LSB

Lower Jurassic deposits are mainly exposed in the southeastern part of the LSB with spectacular outcrops in the low mountain ranges of southern Lower Saxony (Fig. 5). Three sections (Langenberg section, Bisperode section, Osterwald section) crop out south of Hannover, and all of them are well accessible. The Langenberg section can be studied in an active quarry about 5 km east of Goslar, which represents one of the most important Jurassic fossil vertebrate localities in Europe (e.g. Sander et al. 2006). The Bisperode and Osterwald sections are both abandoned quarries located about 2 km southwest of Lauenstein, and about 3 km south of the village of Springe Holtensen, respectively. In addition, the scientific bore hole (Konrad #101 core) was studied, which was drilled close to the village Salzgitter-Beddingen (Fig. 5). In the LSB, the Upper Jurassic strata is represented by the lithological units of the Upper Ornatenton Formation (Fm.) (Callovian–Oxfordian), Heersumer and Korallenoolith Fms. (Oxfordian), and the Upper Korallenoolith and Süntel Fms. (Kimmeridgian). This study specifically focuses on the Oxfordian Korallenoolith Fm. (Middle to Late Oxfordian). The Korallenoolith Fm. is essentially composed of oolithic and bioclastic limestones intercalated with marls and claystones, interspersed with coral patch reefs (Helm et al. 2001). Based on the faunal content and the lithological characteristics, the Korallenoolith Fm. is further subdivided into Lower, Middle, and Upper Korallenoolith (Schulze 1975).
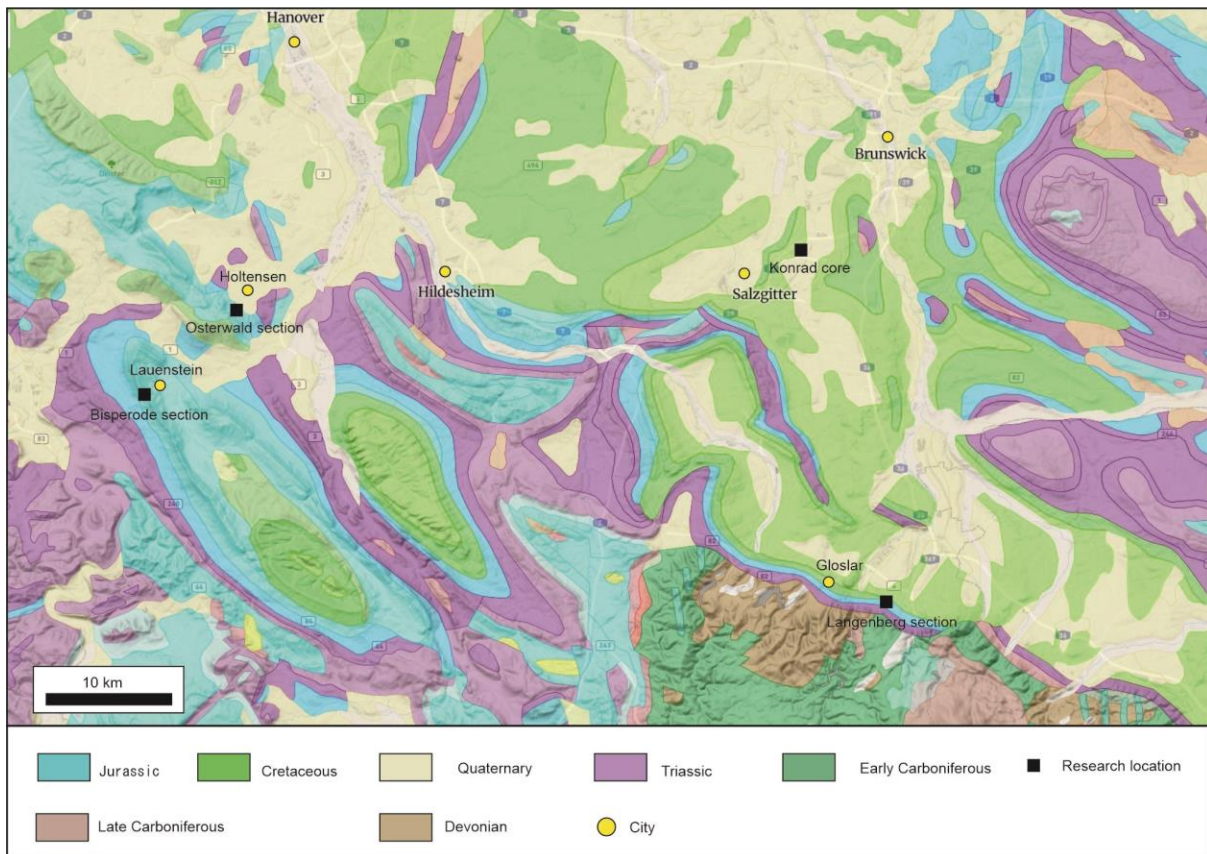
Fig. 5 - Geological map of the study area with the locations studied or used for comparison marked as black squares (modified from Kockel et al., 1996).

1.3.2 Biostratigraphy

The biostratigraphic subdivision of the Upper Jurassic strata in Northern Germany was developed based on ammonites, ostracods, dinoflagellate cysts, charophytes, foraminifera, spores, and pollen (Schudack 1994; Weiß 1995; Gramann et al. 1997; Hardenbol et al. 1998). Due to the rare occurrence of age-diagnostic ammonites, the Oxfordian strata in the LSB is divided based on ostracods with the ostracod zones 1 to 8 covering the Ornatenton (zone 1), the Heersumer Fm. (zones 2 and 3), and the Korallenoolith Fm. (zones 4 to 8). The correlation between the ostracod zones from Gramann et al. (1997) and the sub-boreal ammonite zones is indicated in Fig. 6.

Fig. 6 - Lithostratigraphic scheme of the Late Jurassic and its correlation with the standard zonation of the sub-boreal ammonite province (modified from Schulze 1975; Gramann et al. 1997; Hardenbol et al. 1998; Gradstein et al. 2020) and ostracod zonation (Schudack 1994; Weiß 1995).

1.4 Main objectives

This study focuses on refining the Oxfordian shallow-water deposits' sedimentology and stratigraphy in order to answer the following main scientific questions:

1) What was the carbonate depositional setting of the Korallenoolith Fm. within the LSB during the Oxfordian? Can the sequence stratigraphic pattern observed in the Korallenoolith Fm. be compared and correlated on a larger geographic scale?

2) What is the range of the $^{87}Sr/^{86}Sr$ ratios obtained from well-preserved bivalve shells from the Oxfordian Korallenoolith Fm.? Can the $^{87}Sr/^{86}Sr$ ratios be used to calibrate the existing biostratigraphic schemes on a local or even a global scale? If not, what processes affected the $^{87}Sr/^{86}Sr$ ratios derived from the Korallenoolith shell material?

3) How does the $\delta^{13}C$ stratigraphic trend from the LSB look like? Is the Oxfordian carbon isotope proxy obtained from the LSB useful for correlation with time-equivalent carbon isotope profiles from the Tethyan and proto-Atlantic domains? And what kind of carbon isotope trends and possible excursions can be identified? What are the underlying mechanisms behind the Oxfordian carbon isotope shift?

For this purpose, the following objectives have been defined:

1) Establish a potentially complete high-resolution sedimentary and sequence-stratigraphic framework for the Oxfordian deposits in the LSB. The above-mentioned sequence stratigraphic framework will complement preexisting biostratigraphic markers in order to fine-tune the chronostratigraphic constraint of the LSB. This approach will allow comparing the results collected in the LSB with other datasets from

lower latitude sections located in the Tethyan domain during the Oxfordian.

2) Develop a carbon and strontium isotope stratigraphic record for the Oxfordian succession in the LSB in order to refine the age assignment of the shallow-marine carbonates in the LSB. The carbon and strontium isotope chemostratigraphy will be integrated with sequence stratigraphic and biostratigraphic approaches.

3) The high-resolution $\delta^{13}C$ stratigraphic records from the LSB will be compared with existing carbon isotope curves from Tethyan and proto-Atlantic sites. Identification of the Middle Oxfordian carbon isotope excursion (MOxE) within the Korallenoolith Fm. will prompt a re-evaluation of the nature and origin of the globally observed MOxE.

1.5 General outline of the thesis

This thesis is subdivided into 6 individual chapters. Chapter 1 provides the introduction of the general topic of the thesis, and chapters 2 to 5 represent separate manuscripts, which are in preparation for publication in international peer-reviewed journals (except for chaper 4). Chapter 6 represents the conclusions.

Chapter 2 - Carbonate microfacies and transgressive-regressive sequences of Oxfordian shallow-water limestones (Korallenoolith, Lower Saxony Basin)

This chapter is planned to be submitted to the journal ZDGG. The present manuscript focuses on the shallow-marine limestones and marls of the Bisperode section located ~40 km SW of Hannover. This study provides a detailed carbonate microfacies analysis of the Bisperode section, which forms the baseline for the conceptualization of a reef-bearing carbonate ramp model. Following the accommodation to sediment supply ratio (A/S) concept, three different orders of sequences were distinguished in the studied section, resulting in the recognition of three large-, 8 medium-, and 15 small-scale sequences. The supra-regional correlation of the observed sequences is discussed.

Chapter 3 - First record of the Middle Oxfordian positive carbon isotope excursion within the Korallenoolith Formation, Lower Saxony Basin, Germany

This chapter is planned to be submitted to the journal Terra Nova. In the manuscript, a new high-resolution inorganic carbon isotope record is presented, which stems from a scientific borehole (Konrad #101 core) in the LSB. The $\delta^{13}C$ stratigraphic pattern is compared with existing carbon isotope curves from Tethyan and proto-Atlantic sites. Based on stratigraphic constraints, the Middle Oxfordian carbon isotope excursion (MOxE) can be identified. The new findings are discussed with regard to carbon cycle dynamics and the paleoenvironmental conditions prevailing during the Oxfordian.

Chapter 4 - $^{87}Sr/^{86}Sr$ chemostratigraphy of Oxfordian carbonate deposits, Lower Saxony Basin, Northern Germany

Within chapter 4, the $^{87}Sr/^{86}Sr$ ratios obtained from well-preserved skeletal materials (low-Mg calcite

brachiopods, oysters, echinoderm, *trichites* bivalves, and shell fragments) are presented. A multi-methods approach (morphological examination, cathodoluminescent microscopy, and trace elements) is used to assess the preservation state of the studied shells used for seawater $^{87}Sr/^{86}Sr$ reconstruction. In the following, numerical age constraints obtained from Sr-isotope analysis and regional factors affecting shell $^{87}Sr/^{86}Sr$ variability are discussed.

Chapter 5 - Carbon isotope stratigraphy of an Oxfordian carbonate ramp system, Lower Saxony Basin, Northern Germany

In this chapter, high-resolution $\delta^{13}C$ analyses of bulk carbonate samples from three outcrop sections (Langenberg, Osterwald, and Bisperode) and one scientific borehole (Konrad #101 core) are studied and compared. Based on litho- and biostratigraphic constraints, a $\delta^{13}C$ record correlation is presented for the southern LSB for the Oxfordian interval. The chemostratigraphic data presented in this study enables the refinement of the pre-existing biostratigraphic framework and the establishment of a composite high-resolution $\delta^{13}C$ stratigraphic record. The $\delta^{13}C$ records improve the correlation ability between the western and eastern parts of the LSB. Overall, the new framework also allows to better assess the impact of carbon cycle disturbances on the shallow-marine carbonate systems in the LSB. Chapter 5 will also be submitted to an international peer-reviewed journal.

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2. Carbonate microfacies and transgressive-regressive sequences of Oxfordian shallow-water limestones (Korallenoolith, Lower Saxony Basin)

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2.1 Abstract

During the Oxfordian, the Lower Saxony Basin (LSB) was covered by a shallow epicontinental sea, in which a thick succession of marine limestones and marls was deposited. The scarcity of open-marine biostratigraphic marker fossils and numerous sedimentary gaps make it difficult to correlate strata from the LSB with Oxfordian deposits elsewhere in the world. This study focuses on the Oxfordian Korallenoolith Formation, which is well exposed in the Bisperode section located ~40 km SW of Hannover. The ~126 m-thick section was described bed-by-bed during fieldwork and complemented by 73 thin sections that were analyzed for their carbonate microfacies. Based on differences in allochem and orthochem composition and primary sedimentary fabrics, an integrated log of the Bisperode quarry was constructed. Seven lithofacies types (FTs) and fourteen microfacies types (MF-types) are characterized upon which a reef-bearing carbonate ramp model was built. Following the accommodation to sediment supply ratio (A/S) concept, three orders of sequences are distinguished in the studied section, resulting in the recognition of 3 large-, 8 medium-, and 15 small-scale sequences. The large-scale sequences correlate well to the established sequence-stratigraphic model and the medium-scale sequences point to a possible control of their stacking pattern by Milankovitch long eccentricity cycles. For their part, small-scale sequences were most likely controlled by autocyclic processes. This study is important because it helps to better understand the link between the stacking pattern of Oxfordian strata in the LSB and allocyclic processes, allowing future global chemo- and sequence-stratigraphic correlations.

2.2 Introduction

The Upper Jurassic succession of the Lower Saxony Basin (LSB) has attracted significant interest amongst geologists and paleontologists as the strata contains rich invertebrate and vertebrate assemblages and significant reservoirs suitable for oil extraction (Lotze 1968; Pape 1970; Weiß, 1995; Sander et al. 2006, see also Englich et al. 2017 and references herein). Unfortunately, the scarcity of open-marine biostratigraphic markers, the occurrence of multiple sedimentary gaps, and the poor lateral continuity of the strata make it difficult to build a precise litho- and biostratigraphy that allows correlation within the LSB, and worldwide. During the Oxfordian, the LSB was covered by a shallow epicontinental sea, in which a thick succession of alternating marine limestones and marls was deposited (Ziegler 1990; Betzler et al. 2007; Kästner et al. 2008). Some excellent and undeformed Upper Jurassic sections are exposed along the southern margin of the LSB, including the Langenberg quarry outcrop, which is considered one of the most important fossil vertebrate localities in Europe for the Late Jurassic (Sander et al., 2006).

Up to now, several biostratigraphic, lithostratigraphic, and sequence stratigraphic papers on the Oxfordian Korallenoolith Formation (Fm.) have been published. Helm et al. (1998, 2003, 2006) worked on several sections within the LSB, mainly focusing on coral reefs assemblages. Kästner et al. (2008; 2010) studied eight well-exposed sections of the LSB (Süntel area, Wesergebirge, and eastern part of the Wiehengebirge), providing detailed information about lithofacies and lateral thickness variations of the Oxfordian to basal Kimmeridgian carbonate ramp deposits. In terms of sequence stratigraphy, Bai et al. (2017) interpreted the Eulenflucht 1 core, which is located in the Süntel area, covering Oxfordian to Kimmeridgian strata.

The present study focuses on the shallow-marine limestones and marls of the Bisperode section, which are well-exposed in an abandoned limestone quarry located in the Ith Mountains. Here, the thickness of the Korallenoolith Fm. is estimated as being twice the thickness of most Oxfordian outcrop sections in the LSB. Based on facies variation and gamma-ray logs, Betzler et al. (2007) developed a depositional model for the lower part of the Bisperode section. In a follow-up study by Cäsar (2012), the Bisperode record was compared with time-equivalent sections from the south-eastern LSB. The upper part of the section, assigned to the Kimmeridgian Süntel Fm., was studied by Zuo et al. (2017) using a combined approach including sedimentological observation and stable isotope chemostratigraphy.

This study aims to provide a detailed carbonate microfacies analysis of the Bisperode section, which is the first essential step to propose this section as an Oxfordian reference section for future chemostratigraphic studies. Its exceptional thickness points towards a rather complete Oxfordian shallow-marine record. The newly acquired sedimentological data combined and compared with the previous work of Betzler et al. (2007) and Cesär (2012) allow a better assessment of the depositional environment of the Bisperode section and the LSB filling succession during the Oxfordian.

2.3 Geological setting

2.3.1 Regional geology

The LSB represents a sub-basin of the North German Basin located in Central Europe (Ziegler 1977). During the Late Jurassic, the LSB was bounded by the Ringkøbing Fyn High to the north and the London Brabant, the Rhenish, and the Bohemian massifs to the south (Ziegler 1990). The LSB is described as a 300 km long and 65 km wide Late Jurassic to Early Cretaceous trough, which parallels the northern margin of the Rhenish Massif, and which formed part of an epicontinental sea (Betz et al. 1987; Betzler et al. 2007; Fig 1). The basin-fill comprises a ~4500 m-thick sequence of Upper Paleozoic and Mesozoic strata (Bombien et al., 2012; LBEG 2013). Differential subsidence in the LSB controlled by syn-sedimentary faults and salt tectonics began during the Late Triassic (Betz et al. 1987; Gramann et al., 1997; Hoyer, 1965). Consequently, the deposit thicknesses can vary by tens of meters over short distances (Hoyer 1965). During the Oxfordian, the LSB was located at a paleolatitude of ~35°N, most likely within the subtropical paleoclimatic belt (Smith et al. 1994; Helm et al. 2001), and connected with the Boreal Ocean via the Viking Corridor (Ziegler, 1988).
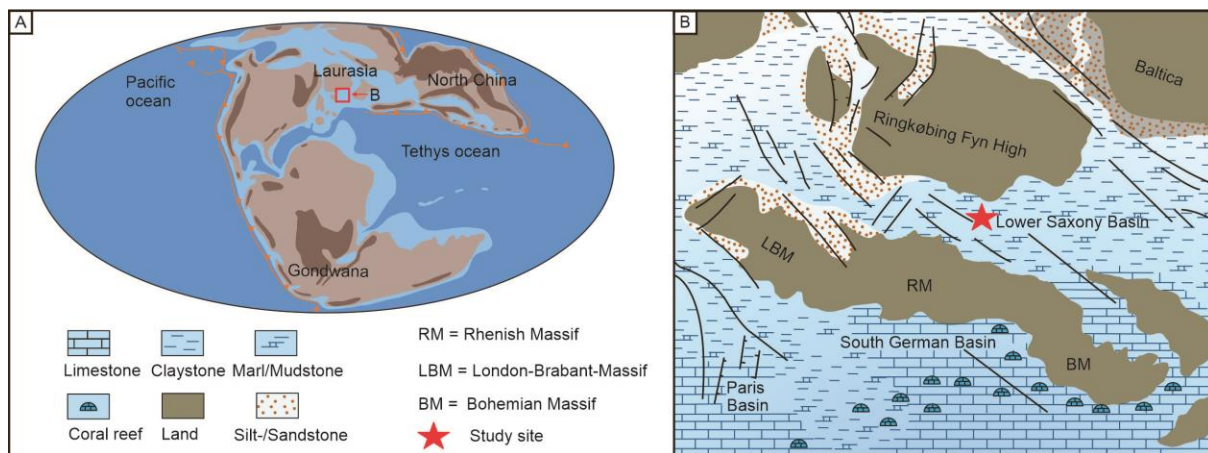
Fig. 1 (A) Global and (B) Central Europe palinspastic reconstruction of the Late Jurassic (152 Ma, modified after Tang, 2021). Major landmasses and general marine facies distribution are shown. RM = Rhenish Massif, LBM = London-Brabant Massif; BM = Bohemian Massif. Map modified after Ziegler (1990). Approximate position of the studied outcrop in the Lower Saxony Basin is marked with a red asterisk.

The Korallenoolith Fm. is restricted to the south-eastern part of the LSB (Gramann et al. 1997) and has been described from many outcrops in the mountainous areas of Lower Saxony including Wiehen- and Wesergebirge, Süntel, Deister, Osterwald, Ith and Subherzynian Basin (Helm et al. 2003). The Korallenoolith Fm. itself consists of oolitic limestones with intercalated bioherms, assigned to a shallow-marine environment with a limited terrestrial influx. Stratigraphically, it belongs to the NW German Malm Group (Helm et al. 2003; Betzler et al. 2007; Kästner et al. 2008; Cäsar et al. 2012; Zuo et al. 2017). Schulze (1975) subdivided the Korallenoolith Fm. into Lower, Middle, and Upper Korallenoolith based on characteristic microfacies assemblages and diagenetic features. More recently, the Korallenoolith Fm. has been subdivided into only two units separated by a well-developed unconformity, the "Hauptemersionsfläche", showing clear evidence of subaerial exposure (Helm 1998; Schülke et al. 2004, Kästner et al. 2008; Cäsar 2012).

2. 3.2 Stratigraphic framework

The biostratigraphic subdivision of the Upper Jurassic in Northern Germany was developed based on ammonites, ostracods, dinoflagellate cysts, charophytes, spores and pollen (Schudack 1994; Weiß 1995; Gramann et al. 1997; Hardenbol et al. 1998). The Oxfordian strata in the LSB is assigned to the ostracod zones 1 to 6 and includes the Ornatenton (zone 1), the Heersum (zones 2 and 3), and the Korallenoolith (zones 4 to 8) Fms. The correlation between the ostracod zones from Gramann et al. (1997) and the Sub-Boreal ammonite zones are indicated in Fig. 2.

Fig. 2 Lithostratigraphic scheme of the Late Jurassic and its correlation with the standard zonation of the sub-boreal ammonite province (modified from Gramann et al. 1997; Hardenbol et al. 1998; Schulze 1975; Gradstein and Ogg 2020) and ostracod zonation (Schudack 1994; Weiß 1995).

Gramann et al. (1997) suggested that the Korallenoolith Fm. covers the interval from the upper *Perisphinctes plicatlics* (*Perisphinctes antecedens* subzone) to the lowermost *Pictonia baylei* ammonite zones. The Bisperode section has been considered to encompass the Lower to Upper Korallenoolith Fm. (Weiß 1995, Mönnig 2002). Weiß (1995) developed a biostratigraphic framework for the upper part of the Bisperode section based on ostracod biostratigraphy, which was refined by Zuo et al. (2017) for the Süntel Fm. forming the uppermost part of the Bisperode section. A stratigraphic assignment is only available for the Upper Korallenoolith ("Humeralis-Schichten"). According to Zuo et al. (2017), the onset of ostracod zone 7 can be placed at 125.5 m (hardground surface). As a consequence, a certain part of the Upper Korallenoolith can be placed within ostracod zone 6, but the lower boundary of zone 6 remains unclear (Cäsar 2012).

The *Florigemma*-Bank reef associations is another stratigraphic marker in the marginal marine facies of the Korallenoolith Fm. From the *Florigemma*-Bank, a few poorly preserved ammonites findings are reported (Helm et al. 1998), further assisting the stratigraphic attribution. The "Hauptemersionsfläche" at or near the top of the *Florigemma*-Bank is the only regional marker bed within the Korallenoolith Fm., which can be traced over a large lateral extent in the Weser-Leine area (Hoyer 1965; Helm 1998;

Kästner et al. 2008). Kaiser (1979) placed the *Florigemma*-Bank of the Hohenstein area (locality "Grüner Altar") in the *Perisphinctes variocostatus* subzone *(Perisphinctes cautisnigrae* ammonite zone), which would indicate an early Late Oxfordian age. In the Bisperode section, the *Florigemma*-Bank and the "Hauptemersionsfläche" are not clearly identified. However, based on their resemblance, many studies suggested that the coral-rich interval (5.0–45.0 m) and the hardground (~50.0 m) described in the lower part of the Bisperode section are equivalent to the *Florigemma*-Bank and the "Hauptemersionsfläche", respectively (Betzler et al. 2007; Cäsar 2012; Bai et al., 2020). In the Bisperode section, the "Hauptemersionsfläche" equivalent (Surface D in Cäsar 2012) is capped by a marly limestone interval (53.0–60.0 m) including the first occurrence of the foraminifera *Alveosepta jaccardi* (Betzler et al. 2007) indicative of the *Ringsteadia pseudocordata* ammonite zone in the LSB (Gramann 1997).

2.4 Methods

2.4.1 Fieldwork, sampling, and facies analysis

The Bisperode section covers shallow-marine carbonate deposits ranging from Oxfordian (Korallenoolith Fm.) to Kimmeridgian (Süntel Fm.) and is accessible in an abandoned quarry (52°04′00.09″N, 9°32′36.47″E) located ~2 km southwest of the village Lauenstein, Lower Saxony, Germany. Limestones of the Korallenoolith Fm. are exposed in a ~126 m-thick succession, showing slightly tilted bedding (Fig. 3). A total of 258 rock samples were taken approximately every 50 cm, accompanied by a detailed lithological description. A total of 73 petrographic thin sections for carbonate microfacies analysis were produced. Carbonate microfacies was analyzed using an Olympus BX53 microscope equipped with an Olympus SC50 camera. The classification scheme of Dunham (1962) with the modifications of Embry and Klovan (1971) was applied.

2.4.2 Sequence stratigraphy

The sequence stratigraphic arrangement follows the concept of accommodation to sediment supply (or production) ratio (A/S) concept (Cross et al. 1993; Cross and Lessenger 1998; Homewood et al. 1999, Schlager 2005; Catuneanu et al. 2011). The A/S ratio controls the facies record and the stratigraphic architectures. Discontinuity surfaces (e.g., hardgrounds, karstified and erosional surfaces, paleosols) help to identify environmental changes (like subaqueous erosion or subaerial exposure) and to understand the changes in A/S leading to hiatuses. Based on the combination of the vertical stacking pattern of microfacies types (MF-types), changes in bed thickness, and the occurrence of diagnostic surfaces, three orders of sequences were differentiated in the studied section, including small-, medium-, and large-scale sequences. The hierarchy between small-, medium-, and large-scale sequences is based upon the significance of facies shift and the magnitude of the deepening/shallowing trends.
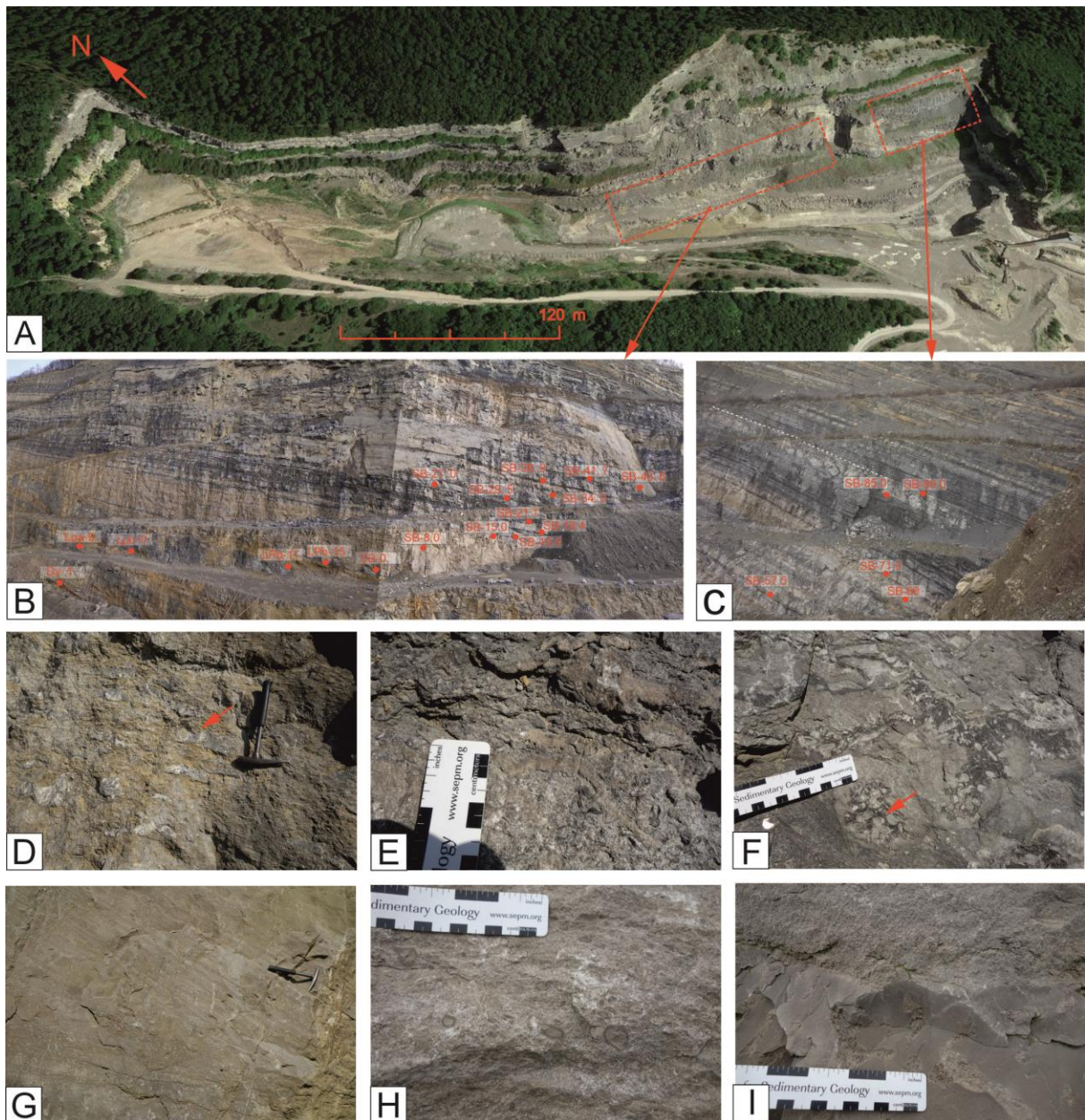
Fig. 3 Field view and selected sedimentary features exposed in the Upper Jurassic succession of the Bisperode section. (A) Aerial view of the Bisperode quarry (Google Earth imagery). (B) and (C) Enlargements of the area defined by the two stippled red boxes marked in (A), which show views of the steep quarry cliff with selected sample positions. (D) Coral-rich boundstone facies containing flat, sheet-like and strongly recrystallized corals (at 22.0 m). (E) Sharp-based bioclastic-rich rudstone with abundant coral fragments showing fining-upward sequences and cross-bedding (at 9.0 m). (F) Stalk-shaped bafflestone bored by bivalves (molds of bivalves) fossilized in life position. Note how the borings are filled with fine-grained material including second generation of bivalve borings (at 31.0 m). (G) Ooid-rich grainstone facies showing well-developed medium-scale cross-stratification (at 40.0 m). (H) Oncoid-rich rudstone including coarse individual oncoids (0.2 to 2 cm) with a distinctive concentric but irregular cortex (between 51.2 to 52.0 m). (I) Well-developed hardground with borings, which corresponds to the white stippled line in (C) and marks the top of the studied section (at 125.5 m).

2.5 Results and interpretation

2.5.1. Lithostratigraphy
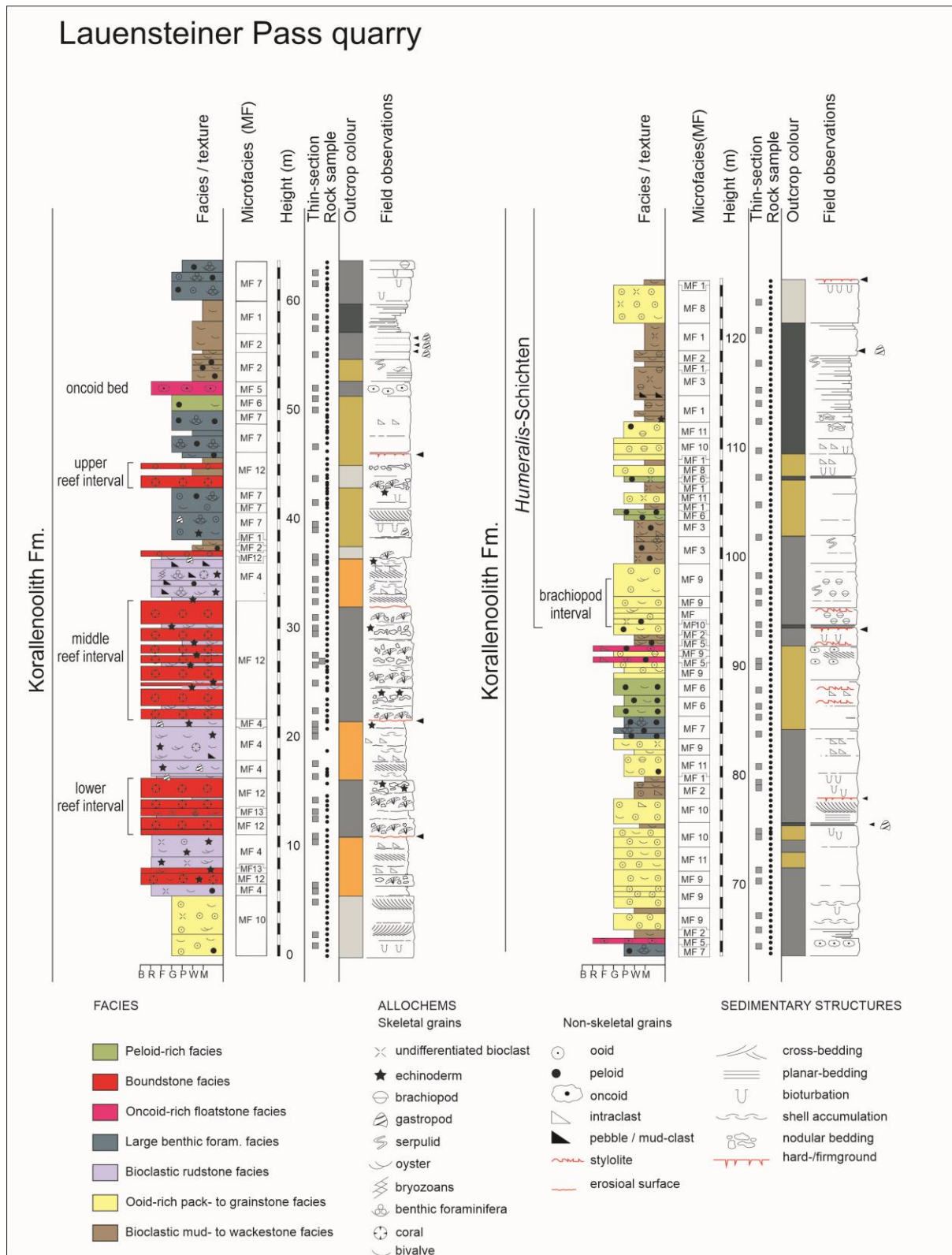
Fig. 4 High-resolution log description of the Bisperode section showing lithology, thin section sample distribution, height (m), and erosional profile.

Here we focus on the lower 126 m of the accessible section (Fig. 4), assigned to the Korallenoolith Fm. (Betzler et al. 2007; Cäsar 2012). The base of the section is characterized by ~5.5 m of ooid-rich grainstones including rare to common iron ooids. The ooid-rich grainstone lithologies belong to the Hauptoolith Member (Mbr.) (Klüpfel 1931; Stinder 1991; Schülke 1993; Helm et al. 2003). Above, five boundstone horizons alternate with bioclastic-rich rudstone between 5.5 and 45.0 m. The top reefal boundstone layer is considered to represent the equivalent of the *Florigemma*-Bank (Cäsar 2012; Bai et al. 2020). Based on different growth forms of corals (ramose, flat sheet-like, dome-shaped, hemispheric), different ecological associations were distinguished by Betzler et al. (2007) and Cäsar al. (2012). Above the middle reef interval, grain- and packstone textures dominate the succession (45.0–65.0 m), with some intervals showing a high portion (>50%) of *Reophacidae cf. Reophax* foraminifera. The marl-limestone alternation intervals at 52.6–60.0 m, 99.5 m–103.5, and 112.5 m–121.5 m are characterized by wacke- to mudstone beds. The upper part of the section (66.0 to 125.5 m) is essentially composed of ooid-rich pack- and grainstones with intercalations of bioclastic-rich wackestone.

2.5.2. Facies types

A total of 7 facies types (FTs) including 14 different microfacies types (MFs) are distinguished for the Bisperode section (Table 1).

Table 1 Facies types and microfacies types in the present study

Facies types (FT)	Microfacies types (MF)	Description	Depositional environment and interpretation	Energy
FT 1 Bioclastic wackestone to mudstone facies	MF 1 Thin-bedded mudstone with bioclastic	This MF-type is gray bioclastic mudstone composed of micrite, rich in argillaceous, quartz, organic matter, and scattered pyrite. The main skeletal components are fine molluscan bioclasts, benthic foraminifera, a few ostracods, and crinoid stem (Fig. 5A, B).	Open marine	Low
	MF 2 Bioturbated wackestone	This MF-type is wackestone containing shell fragments derived from benthic foraminifera, brachiopod, and serpulid. Two types of foraminifera species have different shapes and sizes; the foraminifera chamber is filled with black organic materials, so the chamber structure is unclear. The brachiopod shells microstructure reveals both punctuated (terebratula-like) and nun-punctuated (rhynconella-like) specimens (Fig. 5C).	Open marine	Low to moderate
	MF 3 wackestone with shell fragments	In this MF-type. Bioclasts include shell fragments of juvenile gastropod, echinoderm, and brachiopod shell fragments, and thin filamentous shells representing potential mollusk larval stages (Fig. 5-E). Abundant angular to subangular smaller detrital grains, agglutinated foraminifers, and some organic matters are recognized (Fig. 5D, E).	Open marine	Low to moderate
FT 2 Bioclastic-rich facies	MF 4 Bioclastic	This MF-type is dominated by micritized (coated) bioclasts, which account for >50 % of the particle. The biofabric with imbrication structure and the elongated bioclasts vary in a clear orientation, resulting in very poor sorting. Bioclasts are derived from coral fragments, gastropods, bivalves, echinoderms, brachiopods, and foraminifera; besides, peloids and rare ooids are observed, most grains are cortoids comprising coated bioclasts. Selective dissolution is visible amongst the bioclasts, with some of them showing the original structure, whereas some are just keeping the stable micrite envelops and encrustations (Fig 5F).	Bioclastic sand bar or open marine? storm deposits	Moderate to high

Facies types (FT)	Microfacies types (MF)	Description	Depositional environment and interpretation	Energy
FT 3 Oncoid-rich facies	MF 5 Oncoid-rich rudstone	MF-type 5 is composed of oncoids with distinctive concentric but irregular cortex; Individual oncoids are 2 mm to 20 mm in diameter. The oncoids are elliptical, lobate, and with knobby surfaces, the surface irregular organism-bearing *Bacinella-Lithocodium* laminations. They have formed around gastropods, bivalve fragments, foraminifera, and the shape of the core strongly influences the body of the oncoids. Some of the oncoids show clear signs of compaction and dissolution along their outer face, and serpulid worm tubes within the cortex, some sparry patches (dissolved organism?) within the cortex, and fine-grained sediments are also trapped on the oncoid surface by the organism. The intra-oncoids have a continuous micritic lamination (Fig. 5G, Fig. 5H).	Lagoon, storm events	Moderate
FT 4 Peloid rich facies	MF 6, Bahamite type peloids	With various shapes and sizes, with a relic internal structure and a black lamina envelope surrounding it, these may be heavily micritic bioclasts. Brachiopod fragments are also present (Fig. 5I). The peloids show a typical ellipsoidal shape including in rare occurrences slightly larger particles. The peloids are stained in brown by organic matter, probably fecal in origin (Fig. 6A).	Semi-open lagoon	Moderate
FT 5 Large benthic foraminifera-rich facies	MF 7 Foraminiferal-rich packstone to grainstone	The main component is *Reophacidae cf. Reophax* foraminifera accounts for up to 50% of the total grains. Other bioclasts (~20 %) include fragments of bivalves, brachiopods, and gastropods, as well as the rare crinoid stem. The foraminiferal are large, often exceed 0.5 mm in diameter, and show a complex internal structure, all of them agglutinated ooids or peloids as their wall structure, and their chambers are filled with fine-grained carbonate-mud micirite (Fig. 6B).	Lagoon	Low to moderate
FT 6 Ooid rich facies	MF 8 Radial oolitic grainstone	Aggregate of radial oolitic lithoclasts and radial ooids with grain sizes ranging between 0.4 and 1.75 mm in diameter. They are made up of radial fibrous calcite crystals and weak concentric banding, evenly dispersed within the sparry calcite cement. By the close packing of the ooids, the radial microstructure indicated a quiet water depositional environment. (Fig. 6C).	Oolitic bar	High
	MF 9 Bioclastic oolitic grainstone	This MF-type contains an estimated ooid portion of 80%. Ooids with a tangential structure are present and have different shapes and sizes. Other components are shell fragments derived from bivalves, brachiopods, echinoderms, and agglutinated foraminifera. Few intraclasts and oncoids are also present. Some of the ooids, bioclasts, and oncoids have gone through intensive micritization, but we can still see the original individual structure under the microscope. The interspace between the grains is filled with fine-grained carbonate micrite or sparry calcite cement. The nuclei are entirely calcareous and include opaque micritic grains (peloids) of rather large size compared to the thickness of the cortex (Fig.6D).	Ooids-bioclastic bar	High
	MF 10 Superficial oolitic grainstone	MF-type 11 is grains that are subspherical to subelongated, with the shape being related to the size of the bioclastic nucleus, benthic foraminifera, and gastropods are abundant. Ooids are 0.3 to 0.8 mm in diameter, well-rounded, and show a concentric structure with smaller skeletal or non-skeletal cores. Some ooids show selective dissolution features with dissolution affecting coatings and the ooid cores, and some of them still keep original organic concentric lamination, some are entirely dissolved, and some have completely formed neomorphosed oolite. The interparticle space is filled with sparry calcite. Other components are mainly represented by benthic foraminifers and mollusk fragments (Fig. 6E).	Ooid bar	High

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Facies types (FT)	Microfacies types (MF)	Description	Depositional environment and interpretation	Energy
	MF 11 Oolitic packstone	The ooids have peloidal nuclei and numerous cortical coatings. The nuclei are opaque micritic grains (peloids) of rather large size compared to the thickness of the cortex, and some are micritized bioclastic cores (Fig.6F).	Ooids bar	High
FT 7 Boundstone facies	MF 12 Boundstone	This MF-type is mainly composed of in-situ preserved stromatoporoids and rare scleractinian corals. Between the stromatoporoids or corals space are filled with intraclast containing ooids, echinoid spines, coral fragment, bivalves, gastropods, and rare peloid, which are very poorly sorted. Some coral fragments show bioerosion structures and have been bored by sponges or bivalves and were subsequently filled with fine-grained carbonate sediment—longitudinal sections of the colonial coral show a well-preserved margin, with a slightly thickened wall structure. The stromatoporoid and rare dendritic scleractinian corals underwent selective dissolution, resulting in numerous, partially irregular-shaped vugs. Subsequent hydrothermal dolomitization as indicated by the formation of saddle dolomite can be observed in some vugs. Some vugs were filled by fine-grained carbonate sediment, a well-developed geopetal structure, with black fine lime at the bottom and cementation at the top (Fig. 6G, H).	Reefs, open marine	High
	MF 13 Reef-flank bioclastic	Poorly sorted and densely packed bioclasts in the micritic matrix with mainly remains of sessile benthic organisms, angular to subangular clasts of reworked reefs (coral head), and some bioclasts including skeletal fragments derived from echinoids, bivalves, oysters, bryozoans, and benthic foraminifera (Fig. 6I).	Open marine, or Open lagoon	High

FT-1 – Bioclastic mud-to wackestone facies

Description: FT-1 is characterized by alternating marl-limestone beds between 52.6–60.0 m and wacke- and mudstone beds between 37.0–38.2 m, 65.5–66.5 m, 78.0–80.0 m, 92.0–93.0 m, 99.5–103.5 m, 104.4–105.0 m, 106.0–107.0 m, 108.5–109.0 m, 112.5–121.5 m. Facies type-1 comprises 3 MF-types (MF-1, MF-2, MF-3). Individual marl-limestone couplets show an average thickness of ~30–50 cm and are composed of a brown mud ribbon (marl) and a resistant limestone cap. The brown mud ribbon is made up of clay-and silt-rich marls, typically several centimeters in thickness. The limestone beds of the marl-limestone couplets are 20–30 cm-thick and made up of dark, grey wacke- to mudstones rich in finely disseminated pyrite. The different MFs are distinguished based on the amount and type of bioclastic material, with MF-1 representing a mudstone with small-size bioclasts (Fig. 5A, B). MF-2 corresponds to a bioturbated wackestone with fragments derived predominantly from benthic foraminifera, and brachiopods (Fig. 5C). MF-3 represents a wackestone composed of thin filamentous mollusc shells, echinoderms, and brachiopod fragments (Fig. 5D, E).

Paleoenvironmental interpretation: In FT-1, the dominant mud-and-wackestone texture points to a low hydrodynamic regime supported by the common occurrence of thin filamentous mollusk shells (Flügel, 2004). Moreover, nerineoid gastropods formed semi-sessile communities, which colonized stable seafloor surfaces and maybe grazed on algae or microbial mats in quiet environments. These gastropod communities were sensitive to disturbance and coastal hypoxia (Gallmetzer et al. 2017; Tomašových et al. 2018) and are therefore considered to represent useful paleoecological indicators (Waite et al. 2008).

Mass accumulations of nerineoid gastropods could indicate well-oxygenated mesotrophic conditions prevailing in shallow-shelf sea areas (Schlager et al. 1981; Nebelsick et al. 2019). Based on the above-mentioned sedimentary characteristics and faunal content, FT-1 is best assigned to an outer ramp (open marine) setting with limited water oscillation and including carbonate-dominated storm deposits reworked from inner or mid-ramp settings.
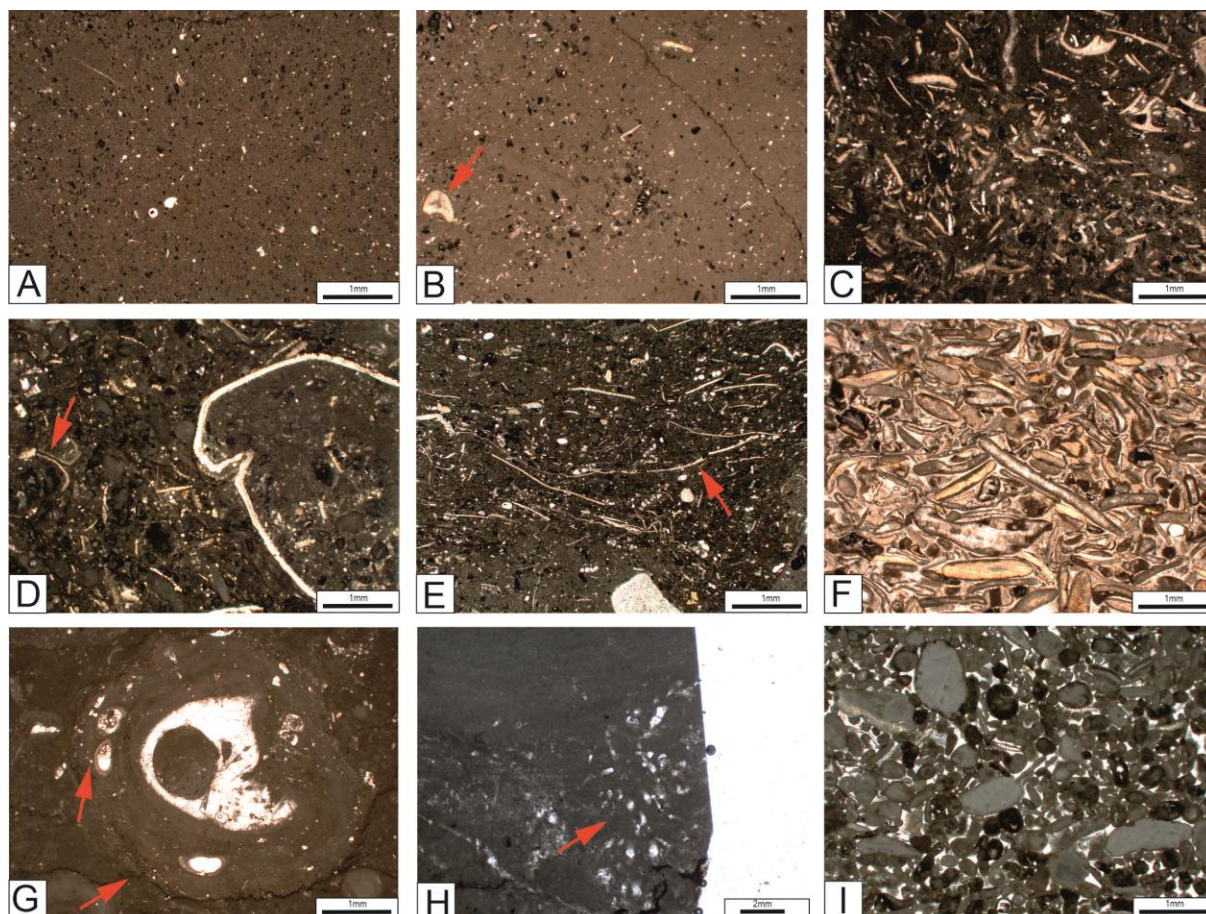
Fig. 5 Oxfordian MF-types defined in the study areas (1). MF-1 Mudstone includes (A) scattered organic matter and pyrite (at 58.5 m) and (B) fine-grain bioclasts of crinoids, ostracods, and foraminifera. The red arrow points at a crinoid arm plate (at 107.5 m). (C) MF-2 bioturbated wackestone, with very common shell bioclast, inlcuding brachiopod shelles, and small benthic forams (at 118.0 m). (D, E) MF-3 bioclastic-rich wackestone including (D) encrusting serpulids (red arrow) and a brachiopod (at 54.4 m); (E) MF-2 bioturbated wackestone with common echinoderm fragments and oriented filamentous bivalve shells (red arrow, at 114.0 m). (F) MF-4 bioclast-rich rudstone with superficially micritized components (at 21.0 m). (G) MF-5 oncoid-rich rudstone with individual oncoids formed around gastropod clasts characterized by crenulated cortices including serpulids (red arrow, at 52.0 m). (H) MF-5 oncoid. Note that the oncoid cortices are composed of crenulated Bacinella-Lithocodium bearing laminations (at 52.0m). (I) MF-6, peloid-, foraminifera-rich grainstone (at 107.5 m).

FT-2 – Bioclastic rich facies

Description: FT-2 occurs commonly in the lower part of the section (5.5–6.5 m, 7.5–11 m, 12.5–13.5 m,

16.3–21.5 m, and 32.5–36.5 m) in the form of massive bioclastic-rich beds (>1 m thickness) often associated with an erosive base (Fig. 5F). FT-2 includes a single MF-type (MF-4). Individual beds typically show fining-upward units and trough cross-bedding. Thin sections reveal that bioclasts are very poorly to fairly sorted from the base to the top of individual beds, often showing a preferred orientation (incl. imbrication structure). The faunal content includes coral fragments, and debris of gastropods, bivalves, echinoderms, brachiopods, and benthic foraminifera, most of the bioclasts being superficially micritized. Secondary allochem grains include peloids, rare ooids (mostly superficial). Moldic porosity is visible among the bioclasts, with some bioclasts showing their original internal structure, whereas others preserve only the stable micrite envelops and encrustations.

Paleoenvironmental interpretation: Large-scale cross-bedding clearly shows deposition above the fairweather wave-base (Betzler et al. 2007). The poor sorting with angular clasts and a high abundance of coral debris indicate that FT-2 was deposited nearby reefal structures. Between 16.3 m and 21.5 m, intense recrystallization of FT-2 is observed, which might support the previous interpretation that this interval has been affected by subaerial exposure as inferred from regional sequence stratigraphic correlation (Betzler 2007; Cesär 2012). Between 32.5 m and 36.5 m, the micrite content increases and indicates transport and redeposition of coarse reworked reef debris within a lower energy environment (Flügel 1982), which is likely to be associated with an open lagoonal setting. FT-2 is interpreted as coarse-grain tempestite reworked from and deposited near coral reefs (Flügel 2004). The composition and high diversity of the fossil assemblage (incl. large echinoderm and coral fragments) indicate a high-energy, open marine environment with normal salinity (Flügel 2004).

FT-3 – Oncoid-rich facies

Description: Oncoid-rich facies (FT-3) occurs in the form of distinct, well-defined, and sharp-based 0.5 to 1 m-thick layers (Fig. 3 H). FT-3 comprises MF-5 only (51.2–52.7 m, 64.9–65.3 m, 90.5–91.5 m). From base to top, the individual beds often show a gradual decrease in oncoid size. Observed micrite-dominated oncoids range from 2–20 mm in diameter and show a predominantly ovoidal shape with an irregular knobby surface. Most oncoid nuclei correspond to gastropods, bivalve fragments, or foraminifera. Locally, serpulids or fine-grained sediment are observed within the cortex. The oncoids are characterized by a distinctive concentric and irregular cortex (Fig. 5G). *Bacinella-Lithocodium*-like oncoids (Védrine et al., 2007; Védrine, 2008) floating in a carbonate-dominated matrix are also observed (Fig. 5H).

Paleoenvironmental interpretation: The composition and lamination types of the oncoids reflect environmental factors that control microbial and algal growth as well as encrusting communities (light, salinity, water energy, sediment input; Flügel 2004). Given the similarity in surface morphology and structure of the cortex, the MF-5 oncoids resemble type-2 oncoids described from the Upper Oxfordian Hauptmumienbank Mbr. of the Swiss Jura (Gygi 2000; Védrine et al. 2007). According to Védrine et al. (2007), this type of micrite-dominated oncoid shows ellipsoidally smooth to lobate growth form and was generated under open-marine and strong wave-energy conditions. In the Hauptmumienbank Mbr., type-2 oncoids preferentially occur around sequence boundaries and transgressive deposits where higher energy conditions prevailed in relatively shallow water. The occurrence of oncoids, as well as the irregular wavy base of the fining-upward rudstone beds, suggest high-energy depositional conditions

most likely triggered by storm activity (Betzler et al. 2007; Cäsar et al. 2012). MF-5 is assigned to a lagoonal depositional environment and influenced by storm-induced bottom currents, able to episodically rework microbially bound and cemented sediments (Wilson 1975; Flügel 2004, Védrine et al. 2007; Betzler et al. 2007).

FT-4 – Peloid-rich facies

Description: FT-4 includes MF-6 and rarely occurs in the section (50.0–51.0 m, 85.5–89.0 m, 103.5–104.5 m). MF-6 resembles the Bahamite peloid type-3 of Flügel (2004) with poorly sorted spherical to ellipsoidal peloids ranging from 0.2–1.0 mm in diameter. Strongly micritized bioclasts with internal structures coated by black lamina are commonly found in association with the peloids. Secondary allochems include benthic foraminifera and brachiopod fragments (Fig. 5-I，6A).

Paleoenvironmental interpretation: Peloid-rich grainstones are a conspicuous constituent of high-energy shallow-marine platform carbonates. The term "Bahamite peloid" (type-3 peloid) was introduced by Gygi (1969) for structureless peloids of Jurassic platform carbonates, which closely resemble peloids found in the interior lagoon of the Bahama banks. This type of peloid originates from intensive micritization of ooids, bioclasts, or aggregation of micrite from disaggregation of calcareous algae leading to the complete loss of the microstructure of the grain.

FT-5 – Large benthic agglutinated foraminifera-rich facies

Description: FT-5 includes a single MF-type (MF-7) occurring at several intervals (38.2–42.5 m, 46.0–50.0 m, 60.0–64.5 m, 83.5–85.5 m). MF-8 is composed of grain- and packstones containing large-size (0.6 cm) agglutinated uniserial Reophacidae cf. *Reophax* foraminifera (> 50%). Other typical components include bivalve (mainly oysters), brachiopod and gastropod shell fragments, rare ooids, as well as peloids and lithoclasts (Fig. 6B). The foraminifera exhibit a complex internal structure, with the individual chambers often being filled with fine-grained carbonate mud. The agglutinated wall structure often contains small-sized ooids, peloids, and bioclasts.

Paleoenvironmental interpretation: In the literature, the genus *Reophax* (Ordovician to present) has been documented in multiple and very different depositional environments such as high-energy shoal deposits (France; Lower Cretaceous; Arnaud-Vanneau 1980), warm-water lagoonal settings (Austria; upper Coniacian; Schlagintweit et al., 2007), and coral-stromatoporoid patch-reef platform margins (Austria; Upper Jurassic; Schlagintweit et al., 2007). In the past, *Reophax* depositional environment reconstruction has been based on the building constituent of the foraminifera test. Following the same strategy, it is possible to infer an open-marine lagoonal depositional environment most likely located nearby some ooid shoals.
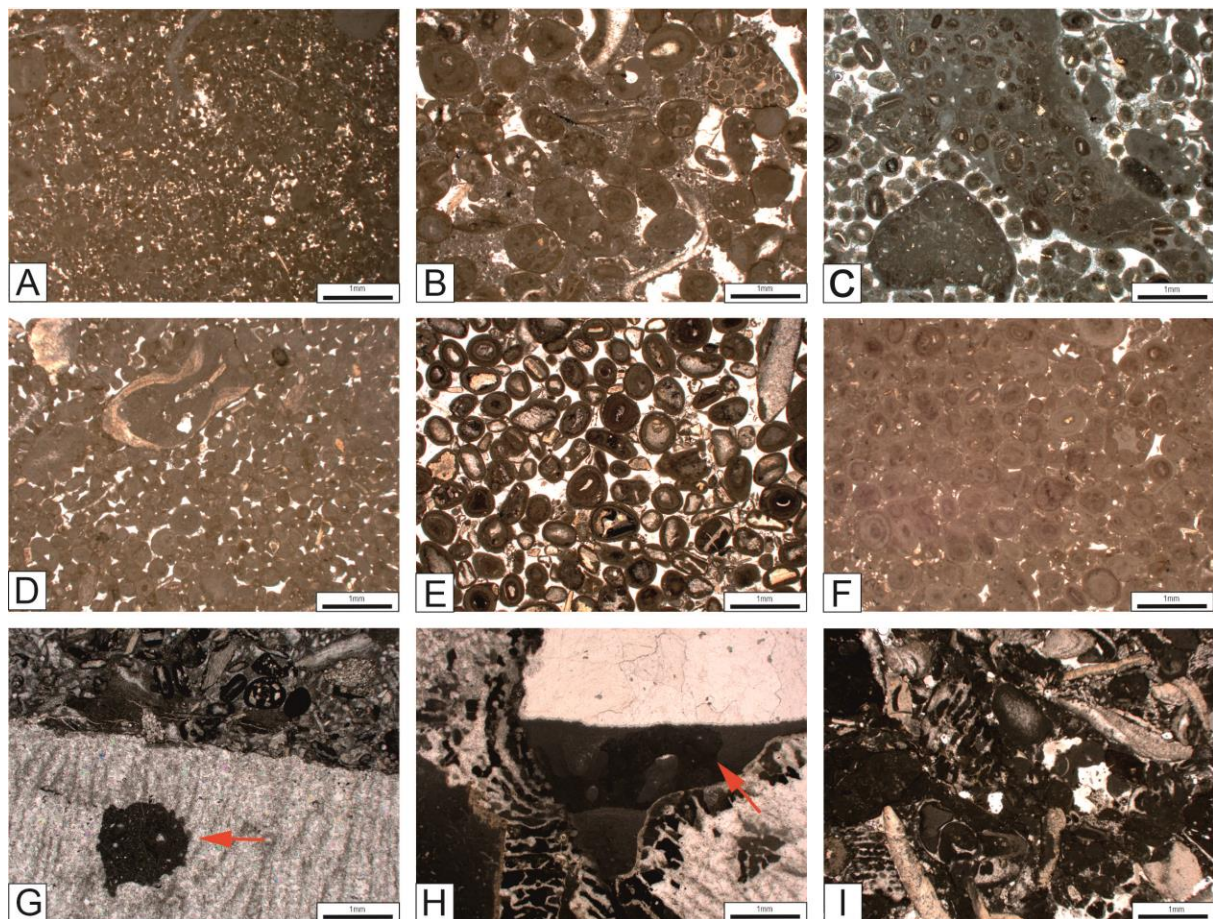
Fig. 6 Oxfordian MF-types defined in the study areas (2). (A) MF-6, peloid-rich packstone, with peloids accounting for more than 50% of all components, with rare ooid and micritised shells (at 51.0 m). (B) MF-7 foraminifera-rich pack- and grainstone, including large benthic Reophacidae cf. Reophax foraminifera (red arrow a) with agglutinated walls composed of peloids, ooids, bioclasts, and lithoclasts (red arrow b) (at 41.5 m). (C) MF-8 ooid-rich grainstone including radial ooids and large ooid-rich packstone intraclasts (at 123.5 m). (D) MF-9 bio-, ooid-rich grainstone dominated by micritized tangential ooids (Bahamite-like ooids, at 104.5 m). (E) MF-10 ooid-rich grainstone, oosparite including ooids showing several growth generations partially iron-enriched (1.0 m). (F) MF-11 ooid-rich pack- to grainstone including Bahamite-like ooids (at 96.0 m). (G) MF-11 coral-rich rudstone belonging to the reef-bearing interval with common boring occurrences (red arrow, at 12.3 m). (H) MF-11 coral-rich boundstone with geopetal fabric (red arrow, at 31.0 m). (I) MF-12 Coral-rich rudstone including large irregular badly sorted coral debris and diverse bioclasts (at 34.5 m).

FT-6 – Ooid-rich pack- and grainstone facies

Description: Oolitic limestones form a significant portion of the lowermost (0.0–5.5 m) and the upper half of the section (66.0–78.0 m, 80.0–83.5 m, 89.0–90.5 m, 90.0–90.5 m, 93.0–99.5 m, 105.0–106.0 m, 107.5–108.0 m, 109.0–112.5 m, 121.5–124.5 m), and are represented by well-sorted, gray or brownish thick limestone beds, often with distinct high-angle cross-bedding (Fig. 3G). Based on ooid type and size, a total of 4 different MFs are distinguished (MF-8, MF-9, MF-10, MF-11).

MF-8 corresponds to ooid-rich grainstones composed of radial ooids ranging between 0.4–0.6 mm in diameter (Fig. 6C). Besides, abundant lithoclasts (up to 8 mm) represent reworked consolidated ooid-

rich packstones. Individual ooids are made up of radial fibrous calcite crystals resulting in a concentric banding and the interparticle pores between the ooids is filled with sparry calcite cement.

MF-9 includes bioclastic ooid-rich grainstones containing ~50 to 80 % ooid grains (Fig. 6D). Individual ooids are relatively small (0.2–0.5 mm) and dominated by concentric ooids. The nuclei often consist of peloids. Additional components include shell fragments derived from bivalves, brachiopods, echinoderms, and agglutinated foraminifera. Secondary allochems include intraclasts and oncoids. Some grains have gone through intensive micritization, but the original structure is still recognizable. The intergranular space is filled with sparry calcite cement.

MF-10 corresponds to ooid-rich grainstones composed of significantly larger-size ooids (0.3–0.8 mm in diameter) than in MF-8; between 0.0–5.5 m iron-rich ooids have been observed. The individual grains have a subspherical or subelongate shape and often show a well-developed concentric rim around the bioclastic nucleus (Fig. 6E). Other components include primarily benthic foraminifers and mollusk fragments. Some ooids show selective dissolution features, which affect both the coatings and ooid cores. Some still keep the original concentric lamination, some are entirely dissolved, and some represent wholly formed neomorphic ooids.

MF-11 includes bioclastic-, ooid-rich packstone, with individual ooids showing mostly peloidal nuclei and numerous cortical coatings (Fig. 6F). Ooids are well-sorted and range between 0.3–0.8 mm in diameter. Nuclei are of relatively large size compared to the thickness of the cortex. The interparticle pores were filled with fine-grained calcareous mud, with only a few pores being filled with sparite.

Paleoenvironmental interpretation: Ooids typically form in Ca oversaturated, agitated shallow-marine subtropical waters influenced by waves and currents above the fairweather wave-base (Tucker and Wright, 1990; Flügel, 2004). Regular sorting, lack of bioturbation, and abundant large-scale cross-bedding support a high-energy depositional setting (oolitic bar). Radial aggregate ooid-rich grainstone (MF-8) is restricted to an interval in the uppermost part of the section (121.5 m – 125.5 m). Radial ooids are more abundant in relatively lower-energy shallow-marine settings (Strasser 1986; Diaz et al., 2019). Oolitic and bioclastic shoals commonly separate more restricted lagoonal environments from deeper ramp environments and may act as wide and extensive barriers to currents and waves (Flügel, 2004).

FT-7 – Boundstone facies

Description: In the lower part of the studied section, coral-stromatoporoid boundstones (FT-7) represent the main portion of the succession (Betzler et al. 2007) and occur in the form of several, often m-thick stratiform layers (e.g., 6.5–7.5 m, 11.0–12.5 m, 13.5–16.3 m, 21.5–32.0 m, 36.5–37.0 m, 42.8–46.0 m). These layers show distinct variations in terms of texture and dominant builders. FT-7 is composed of two MFs, including coral boundstone facies (MF-12) and patch-reef flank bioclastic facies (MF-13). The lower boundstone intervals (11.0–12.5 m, 13.5–16.3 m) are dominated by flat, sheet-like, and strongly recrystallized corals (Fig. 3D, E). Between 6.5–7.5 m platy corals in growth position are embedded in fine-grained micrite (Fig. 3D). Stalk-shaped bafflestones dominate the thick interval between 21.5–32.0 m with distinct bioerosional structures (Fig. 3F). The latter include distinct circular borings produced by bivalves. Often, the bivalves are preserved in life positions with intact shells. Borings have been filled with fine-grained sediment, and certain bivalves have been rebored by other organisms. The

boundstone interval between 42.8–46.0 m is composed of dome-shaped to hemispheric patch-reef structures, surrounded by a debris apron. This interval of the reef facies has been interpreted to be equivalent to the *Florigemma-Bank* (Cäsar 2012; Bai et al. 2020).

MF-12 is mainly composed of in-situ preserved stromatoporoids and rare dendritic scleractinian corals. The space between the stromatoporoids or corals is filled with coarse-grained and poorly sorted debris containing ooids, echinoid spines, coral fragments, bivalves, gastropods, and rare peloids. Certain coral fragments show bioerosion structures and have been bored by sponges or other organisms (Fig. 6G). The resulting cavities were subsequently filled with fine-grained carbonate sediment. In some layers, the stromatoporoid and rare dendritic scleractinian corals underwent selective dissolution, resulting in numerous, partially irregular-shaped vugs. Some dissolution vugs were partially filled by fine-grained geopetal carbonate sediment (Fig. 6H). Saddle dolomite cement filled the residual pore space of these vugs.

Paleoenvironmental interpretation: The reef structures of the Bisperode section did provide a suitable environment for highly diverse reef-dwelling fauna (incl. lithophaga, bivalves, oysters, gastropods, echinoids), indicative of normal-marine conditions. The occurrence of reworked reefal rubble and erosional surfaces indicates episodic storm events. The coarse-grained bioclastic texture of reef-flank deposits implies that the hydrodynamic conditions were sufficient to wash out any fine-grained lime mud (Fig. 6I). The water depth of this depositional environment was probably at or around the fair-weather wave base and the reef structures were located in a mid-ramp setting (Dupraz and Strasser 2002; Carpentier et al. 2007; Betzler et al. 2007).

2.5.3 Depositional model

Based on the facies distribution and previous research on the Korallenoolith Fm. (Helm 1998; Betzler et al. 2007; Cäsar 2012; Bai et al. 2020), a gently inclined carbonate ramp morphology is inferred (Fig. 7).
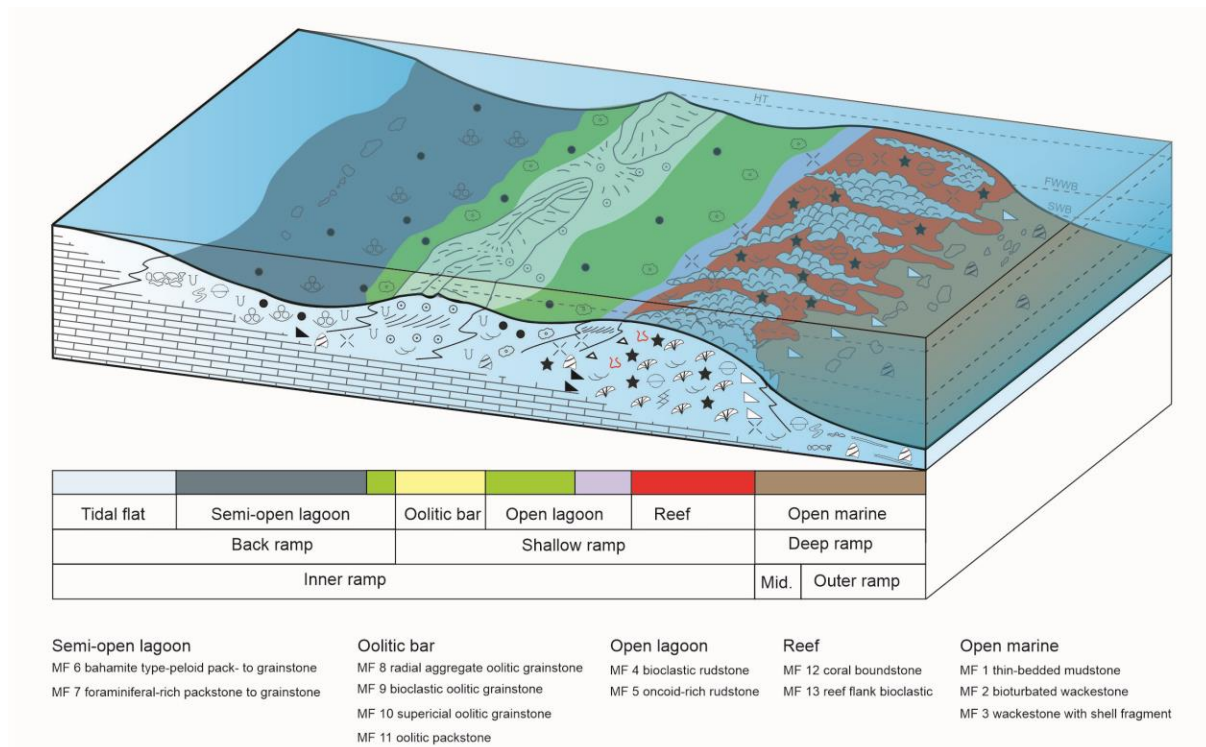
Fig. 7 Conceptual depositional environment model used for the sequence stratigraphic interpretation of the Bisperode section.

Five main depositional environments are differentiated throughout the section based on their characteristics and vertical distribution. A proximal/distal transect includes the following juxtaposed environments: open marine, patch reef, open lagoon, shoal, and semi-open lagoon. This proximal/distal succession reflects a hydrodynamic energy gradient. The open marine facies deposited below the storm wave-base is characterized by a large proportion of fine grain-size particles within a micrite matrix. The main textures are wackestone and mudstone, which formed the marl-limestone couplets bed with abundant bioturbation, indicating very low energy conditions. Stenohaline organisms (e.g., brachiopods and echinoderms) are indicative of normal-marine conditions (Strasser et al. 2012; MF-1, MF-2, MF-3). The patch-reef depositional environment is mainly composed of coral-rich boundstones and embedded reefal debris, reflecting a high-energy environment and isolating a lagoon from the open ocean. In this transitional zone (between open marine and open lagoon), storm waves and storm-induced currents lead to abrupt changes by redistributing sediment in large quantities, and by reworking corals (Flügel 2004; Strasser et al. 2012; MF-12, MF-13). Open lagoon facies deposited behind the reefs are characterized by diverse normal-marine fossils (bioclastic-rich rudstone, MF-4) deposited during episodic storm events. Oncoids were formed in the open lagoonal environment and subsequently reworked and redeposited during episodic storm events (MF-5). The oolitic bar corresponds to a higher energy environment with a high lateral variability due to tidal and long-shore currents. Some inlets cut through the sand bar and allow tidal currents to transport sediment and water into and out of the lagoon (Védrine and Strasser 2009). The texture is dominated by ooid-rich grainstone, confirming constant high-energy conditions (MF-8, MF-9, MF-10, MF-11). A semi-open lagoon, characterized by more restricted conditions with higher salinity, might have formed behind the high-energy facies of the oolitic

bar. Foraminiferal-rich peloid packstone-to-grainstone implies a low-energy environment with rare ooids washed in from the oolitic bars (MF-6, MF-7).

2.6 Sequence analysis

2.6.1 Small-scale sequences

Throughout the studied stratigraphic section, a total of 15 small-scale sequences were recognized with thicknesses ranging from 2.0 to 15.0 m (Fig. 8). The lowermost small-scale sequence (SS-1) is formed by thick-bedded, partly cross-bedded, oolitic-rich grainstones (0.0–5.5 m) interpreted as a regressive hemisequence including the stacking of coarsening upward trends (Betzler et al. 2007). The overlying SS-2 (5.5–12.5 m), SS-3 (11.0–21.5 m), and SS-4 (21.5–36.5 m) represent the superposition of deepening-shallowing hemisequences characterized by the transition from bioclastic rudstone facies (MF-4) at its base, grading upward into reef deposits (MF-12 and MF-13) back to bioclastic rudstones. The top of SS-3 is bound by a pronounced iron-stained exposure surface (surface B+C in Cäsar 2012) characterized by microkarst structure. SS-4 contains the most common occurrence of coral-rich boundstone over a ~10 m-thick interval and corresponds to the "middle reef interval" (Betzler et al. 2007). SS-4 is capped by a sharp erosional surface recognized as well in Betzler et al. (2007). SS-5 (36.5–43.0 m) and SS-6 (43.0–51.2 m) show a very similar thickness and composition made up of coral-rich boundstone at the base grading upward into the foraminifera-rich pack- and grainstones. SS-6 includes the last occurrence of coral-rich boundstone in the section interpreted as the top of the *Florigemma-Bank* equivalent (Cäsar 2012; Bai et al., 2020) or the "upper reef interval" of Betzler et al. (2007). SS-6 is capped by an erosion surface correlative to the "Hauptemersionsfläche" based on its stratigraphic positioning (capping the coral boundstone-rich interval) and its gamma-ray signature (Betzler et al. 2007; Cäsar 2012; Bai et al. 2020). The overlying SS-7 (51.2–65.0 m) is characterized by transgressive and regressive hemisequences grading from an oncoid-rich rudstone into open-marine deposits (MF-1 and MF-2) evolving upward into the foraminifera-rich pack- and grainstones, respectively. The interval between 52.6–57.6 m contains some abundant, up to 3 cm-long nerineoid gastropods. In this interval, pronounced nodular bedding composed of individual ovoid-shaped nodules is prevalent. SS-7 is capped by a firmground (Surface E; Cäsar 2012) including intense bioturbation, possibly indicative of reduced sedimentation rates associated with a transgressive surface. SS-8 (65.0–75.5 m), SS-9 (75.5–78.0 m), SS-10 (78.0–90.5 m), and SS-11 (90.5–100.0 m) constitute the ooid-rich grainstone (MF-8 to MF-11) interval of the section. Their transgressive and regressive hemisequences depict a facies belt migration from an oolitic bar into open-marine conditions back to an ooidal bar. SS-10 shows a slight difference with more regressive semi-open lagoonal deposits (MF-6 and MF-7). Each sequence is separated by distinctive surfaces interpreted as hardgrounds based on the strong bioturbation and fossil density and the common occurrence of dark-coloured mineralization. Noteworthy, the top of SS-9 and SS-10 correspond to surfaces F and G from Cäsar (2012). SS-12 (100.0–106.0 m), SS-13 (106.0–108.5 m), SS-14 (108.5–112.5 m), and SS-15 (112.5–125.5 m) show similar composition and facies belt fluctuations than SS-8 to SS-11, but with thicker mud- to wackestone intervals (MF-1 to MF-3)

characteristic of the *Humeralis Schichten*. Apart from the top of SS-15, which is characterized by a karstified surface, the other sequence boundaries are unspecific.
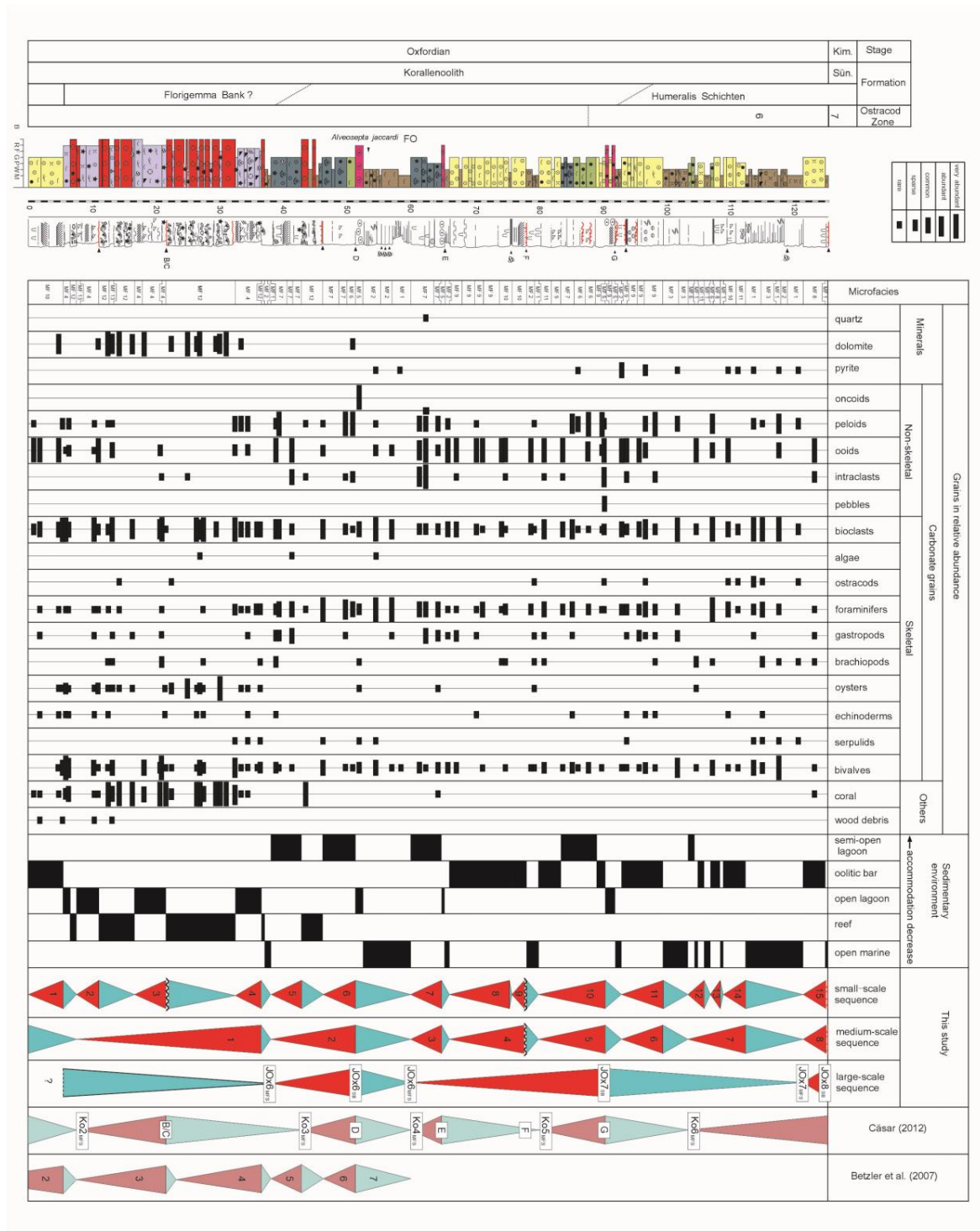

Fig. 8   Sedimentological description, depositional settings and sequence stratigraphic interpretation of the Bisperode section including semi-quantitative allochem composition.

2.6.2. Medium-scale sequences

Eight medium-scale sequences (MS) were recognized, showing a thickness range from 6 to 32 m. The number of SS sequences per MS sequence varies from 1 to 4. MS-1 (0.0–39.0 m; SS-1 to SS-4) is the thickest MS recorded in the Bisperode section and starts with a transgressive hemisequence depicting a facies shift from MF-11 to MF-13. Its regressive hemisequence includes most of the coral-boundstone interval and starts and finishes with MF-13 corresponding to an aggradational stacking pattern indicating that A/S roughly equals one. The MS-2 (39.0–51.2 m; SS-5 and SS-6) transgressive hemisequence corresponds to a shift from MF-13 to MF-1 and marks the first occurrence of the most distal facies recorded in the Bisperode section (MF-1). The MS-2 regressive hemisequence starts with MF-1 and is capped with the erosional surface (51.2 m) interpreted as the "Hauptemersionsfläche" (Betzler et al. 2007; Cäsar 2012; Bai et al. 2020). The MS-3 (51.2–65.0 m; SS-7) transgressive hemisequence is the second thickest transgressive interval composed of the most distal facies MF-2 and MF-1, which indicates one of the smallest A/S ratios of the entire section. Its regressive hemisequence is the thinnest described in the Bisperode section and corresponds to a facies shift from MF-1 to MF-8 within less than 5 m. The MS-4 (65.0–78.0 m; SS-7 to SS-9) transgressive hemisequence corresponds to a facies shift from MF-7 to MF-2. Its regressive hemicycle marks the reapparition of ooid-rich grainstones after a ~60 m stratigraphic gap. MS-5 (78.0–90.5 m) and MS-6 (90.5–100.0 m) are equivalent to SS-10 and SS-11 and the regressive hemisequences depict a facies shift from MF-1 to MF-11 and MF-2 to MF-9, respectively. The *Humeralis Schichten* include MS-7 (100.0–112.5 m; SS-12 to SS-14) and MS-8 (112.5–125.5 m; SS-15). The MS-8 transgressive hemisequence is the thickest and includes the most distal facies (MF-1 and MF-2), which indicate the lowest A/S values.

2.6.3 Large-scale sequences

Three large-scale sequences (LS) with an average thickness of ~45 m are recognized in the Bispeorde section. All LS show a similar amplitude of facies belt migration interpreted to range from subaerial exposure to open-marine depositional environments. LS-1 (0.0–51.2 m; MS-1 to MS-2) is the thickest LS recorded in the Bisperode section. The base of LS-1 is not accessible in the studied area but is interpreted to correspond to the transition between the Heersum and the Korallenoolith Fms. Its regressive hemisequence ends with the sharp erosional surface (51.2 m) interpreted as the "Hauptemersionsfläche" (Betzler et al. 2007; Cäsar 2012). The LS-2 (51.2–90.5 m; MS-3 to MS-5) transgressive hemisequence corresponds to the first occurrence of a thick (> 5 m) interval of deposits characteristic of an open-marine depositional environment. The top of LS-2 corresponds to the hardground correlative to the surface G of Cäsar (2012) located 7.5 m below the base of the *Humeralis Schichten*. LS-3 (90.5–125.5 m; MS-6 to MS-8) covers the entire *Humeralis Schichten*. The LS-3 transgressive hemisequence is characterized by the progressive thickening of open-marine deposits from MS-6 (1.0 m), MS-7 (3.0 m) and MS-8 (8.0 m) transgressive hemisequences. The LS-3 transgressive hemisequence is interfingered with MS-6 and MS-7 regressive hemisequences including ooid-rich grainstone shoreface deposits. This trend of progressive thickening of transgressive hemisequences indicates an overall increase of the A/S ratio with the largest value reached at 122.0 m.

LS-7 ends at 125.5 m which corresponds to the karstified surface characteristic of the top of the *Humeralis Schichten*.

2.7 Discussion

Sequence-stratigraphic regional and supra-regional correlations

Betzler et al. (2007) suggested a subdivision of the lower part of the Bisperode section (0.0–60.0 m) into 7 "long-term" sequences, a scheme showing minor divergences with the present interpretation. Comparatively, the follow-up study from Cäsar (2012) subdivided the exposed Oxfordian strata of the Bisperode section into 6 sequences (Ko1 to Ko6; Fig. 8) of which one (Ko1) is not accessible anymore and therefore, is not described in this study. Ko2 to Ko6 broadly correlate with our LS-sequences LS-1 to LS-3. The differences between Cäsar (2012) and our study is due to the fact that Ko2 and Ko3 as well as Ko4 and Ko5 have been merged into our LS-1 and LS-2, respectively. The last difference and probably the most significant one is the interpretation by Casar (2012) of the mud-dominated intervals at 51.2–60.0 m and 112.5–122.0 m to be supratidal and open- to restricted-lagoon depositional environments respectively. A supratidal origin for the interval 51.2–60.0 m is unlikely based on the presence of ooids and marine fauna (e.g., oysters) revealed by our MF-analysis within this interval. Concerning the strata between 112.5–122.0 m, the occurrences of stenohaline organisms such as brachiopods and echinoderms do not support the interpretation of a restricted-lagoon depositional environment for this interval. However, the interpretation of possible open-marine lagoon deposits cannot be ruled out. A more conservative approach is applied in this study by considering both intervals to be formed in a similar depositional environment based on their sedimentological characteristics and their resemblance with the mud-dominated interval located between 100.0–103.5 m interpreted in here and in Cäsar (2012) as open marine deposits.

According to the sequence-stratigraphic chart of Hardenbol et al. (1998), the Late Jurassic was characterized by a second-order transgressive trend starting in the *Quenstedtoceras mariae* (lowermost Oxfordian; $JOx1_{SB}$) and ending in the *Aulacostephanus euxodus* (uppermost Kimmeridgian; $JKi6_{MFS}$) ammonite zones, respectively. The latter second-order trend was subdivided, in the Oxfordian, into 8 higher-order sequences with five major sequence boundaries (SBs) recorded within the *Q. mariae* ($JOx1_{SB}$), the uppermost *P. plicatilis* ($JOx5_{SB}$), the uppermost *P. cautisnigrae* ($JOx6_{SB}$), the *R. pseudocordata* ($JOx7S_B$), the lowermost *P. baylei* ($JOx8_{SB}$) and four major maximum-flooding surfaces (MFSs) documented within the uppermost *P. mariae* ($JOx1_{MFS}$), the *P. cautisnigrae* ($JOx5_{MFS}$), and the lower and upper *R. pseudocordata* ($JOx6_{MFS}$ and $JOx7_{MFS}$). Maximum regressive surfaces (MRSs) and MFSs ages are expected to be diachronous in each basin due to their strong dependence on sedimentation supply and regional subsidence change. Subaerial unconformities (SUs) on the contrary are much more reliable as chronostratigraphic markers since they are defined as the onset of base-level fall (Csato and Catuneanu 2012; Krencker et al. 2022). In the Bisperode section, we propose that no/or a reduced Lowstand Systems Tract and a Falling Stage Systems Tract are preserved following the assumption from Betzler et al. (2007). This implies that SBs documented in our work coincide with SUs. Even though the accurate dating of the Korallenoolith Fm. is still challenging, it is interesting to notice

that some of the key stratigraphic markers of the LSB and our large-scale SBs can be correlated to Hardenbol et al. (1998) sequence-stratigraphic chart. This indicates that eustatic sea-level fluctuations were likely the main driver behind the building of at least the LS-sequences recorded in the Bisperode section despite different subsidence and sediment supply histories specific to each basin.

First, in the LSB the Callovian/Oxfordian transition is described as an erosional surface cutting through the offshore claystone from the Ornatenton Fm., which in the south-eastern part of the basin is directly overlain by the shallow-marine Korallenoolith Fm. (Mönnig 1989; Fischer 1991). The timing and the nature of this regionally-significant surface match well $JOx1_{SB}$ characteristics. Second, even though the transition from the Heersum to the Korallenoolith Fm. is diachronous between Wesergebirge and the Heersum type section (Siegfried 1954; Stinder 1991), it is noticeable that the major sedimentological change from outer ramp (Heersum Fm.) to inner ramp (Korallenoolith Fm.) depositional setting is recorded around the uppermost *P. plicatilis* zone (Siegfried, 1954) at the Middle/Upper Oxfordian boundary correlating to $JOx5_{SB}$. The "Hauptemersionsfläche" (Kästner et al., 2010) ($LS-1_{SB}$ in this study) is capping the coral-rich boundstones interval, which might correspond to the *Florigemma Bank* (Cäsar 2012; Bai et al. 2020). Following this interpretation implies that the "Hauptemersionsfläche" belongs to the uppermost *P. cautisnigrae* zone (see chapter 2.1), similar to $JOx6_{SB}$. This interpretation is in agreement with the chemo- and sequence stratigraphy of Bai et al. (2017; 2020). The interval located between $LS-1_{SB}$ (surface D, Cäsar 2012) and $LS-3_{SB}$ belongs to the *R. pseudocordata* zone based on the occurrence of *A. jaccardi,* and *Galliaecytheridea dissimilis* and *G. mandelstami*, at 53.0 and 125.5 m, respectively. Our LS-sequence-stratigraphic analysis indicates two remaining SBs within this interval at 90.5 and 125.5 m corresponding to $LS-2_{SB}$ and $LS-3_{SB}$, respectively. $LS-2_{SB}$ and $LS-3_{SB}$ could correlate to $JOx7_{SB}$ and $JOx8_{SB}$ based on their sedimentological characteristics and chronostratigraphical assignment (Hardenbol et al. 1998).

Last but not least, a duration of ~3.8 Myr can be suggested based on the GTS2020 (Hesselbo et al. 2020) for the deposition of the Korallenoolith Fm. dated from the base of the *P. antecedens* subzone (158.6 Ma) to the top of the *R. pseudocordata* zone (154.8 Ma). Assuming an equal duration of the 8 MS-sequences, and acknowledging that the transition between the Heersum and the Korallenoolith Fms is missing in the Bisperode section, an average duration in the order of the long eccentricity cycle (i.e., 405 kyr) can be deduced for these sequences. This suggests that MS-sequences are in line with the scheme proposed by Gygi (2000c) and ultimately that those sequences could be driven by orbital forcing. Even though it is clear that the calculation of the duration is subject to many caveats (e.g., stratigraphic gaps) it is still interesting to see that the obtained result is compatible with Milankovitch cycles as potential controlling mechanism of the MS-sequences. This interpretation is also in line with the sequence-stratigraphic interpretation of the Upper Oxfordian–Kimmeridgian succession in the southern German Jurassic Basin by Ruf et al. (2005), who suggested that their medium-scale sequences (3–10 m-thick) reflect the long eccentricity as well. Altogether, MS- and LS-sequences tend to indicate a potential control of allocyclic processes on their stacking pattern.

2.8 Conclusions

Based on detailed field observations, slab, and thin section analysis, a total of seven superordinate facies types - composed of 14 different microfacies types - were distinguished in the Bisperode section and attributed to different paleoenvironments. Through the paleoenvironmental analysis, a homoclinal ramp setting composed of different juxtaposed facies belts, ranging from semi-open lagoonal to open marine settings, is supported. On the basis of microfacies, diagnostic bedding surfaces, and the vertical lithofacies stacking pattern, a total of 15 small-, 8 medium-, and 3 large-scale sequences are identified. Detailed facies analysis and sequence stacking pattern of the Bisperode section suggest that eustatic fluctuations might have controlled the medium- and large-scale sequences preserved within the Korallenoolith Fm. based on their good match with the well-established eustatic model (e.g., Hardenbol, 1998). Regional synsedimentary salt tectonism and sedimentation rate fluctuations may have played a role in relative sea-level changes in the LSB and as such influence most of the small-scale sequences. Although it is clear that the lack of strong biostratigraphic markers hampers the confidence in the correlation between regional and global sequence-stratigraphic model in the LSB, this work provides a general framework, which will help to better understand the link between the stacking pattern of Oxfordian strata in the LSB and allocyclic processes allowing future chemo- and sequence-stratigraphic correlations.

2.9 Acknowledgments

2.10 References

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3. First record of the Middle Oxfordian positive carbon isotope excursion within the Korallenoolith Formation, Lower Saxony Basin, Germany

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3.1 Abstract

The Middle Oxfordian *Transversarium* ammonite Zone is characterized by pronounced changes in the carbon isotope ($\delta^{13}C$) trend, recorded from various marine and terrestrial organic and inorganic substrates. These carbon isotope events have been associated with climate fluctuations, changes in marine carbonate production, and long-term sea-level rise. A new high-resolution inorganic $\delta^{13}C$ record illustrating the same chemostratigraphic feature is obtained from a scientific borehole (Konrad #101 core) located in the Lower Saxony Basin (LSB). The record is interpreted to reflect synchronous changes in the global marine dissolved inorganic carbon pool, probably in response to Middle Oxfordian reef proliferation caused by climatic changes. This is the first record of the Middle Oxfordian positive $\delta^{13}C$ excursion within the Korallenoolith Formation in the LSB. Our high-resolution data set prompts a re-evaluation of the nature and origin of Middle Oxfordian $\delta^{13}C$ excursions.

Keywords: Chemostratigraphy, Oxfordian, Carbon stable isotope, Boreal Realm, Middle Oxfordian MOxE

3.2 Introduction

The Oxfordian stage (Late Jurassic; 161.5–154.8 Myrs, Gradstein et al. 2020) was a time interval of widespread and significant changes in climate, sea-level, and marine sedimentation patterns and associated with marked fluctuations of the global carbon isotope ($\delta^{13}C$) trend (Padden et al. 2001, 2002; Dromart et al, 2003a; Rais et al. 2007; Louis-Schmid et al. 2007a). A pronounced positive carbon isotope excursion (CIE) has been identified in the Middle Oxfordian (Jenkyns 1996; Weissert and Mohr 1996; Padden et al. 2001, 2002; Rais et al. 2007; Louis-Schmid et al. 2007a, 2007; O'Dogherty et al. 2018; Eltom et al. 2018; Carmeille et al. 2020; Eldrett 2022), recorded in both pelagic and shallow marine ramp carbonates. However, with a few exceptions, most of these records are from the Tethyan realm (Cramer and Jarvis 2020, Eldrett 2022). Due to this spatial restriction, combined with often low sample density, and poor biostratigraphic control, the global $\delta^{13}C$ trend across this interval still remains equivocal. In order to explore temporal changes in the isotopic composition of the global marine dissolved inorganic carbon pool during the Late Jurassic, additional and continuous high-resolution stable carbon isotope of the carbonate phase ($\delta^{13}C$) are needed.

During the Late Jurassic, the Lower Saxony Basin (LSB) was located in the Boreal realm and characterized by continuous shallow-marine carbonate deposition (Gramann et al. 1997) (Fig.1). An ostracod biostratigraphic scheme enables correlation of the Oxfordian strata in the LSB with the Boreal standard ammonite zonation (Schudack, 1994; Weiß 1995; Gramann et al. 1997). The few existing stable isotope studies on Oxfordian LSB strata suffer from limited biostratigraphic control and ambiguous stratigraphic $\delta^{13}C$ trends (Kästner et al. 2008; Bai et al. 2017), which limits regional calibration of carbonate strata and global correlations. Here, a high-resolution carbonate $\delta^{13}C$ record from a scientific drill core (Konrad #101 core) is presented and compared with other existing records collected from Tethyan and proto-Atlantic sites, in order to better understand the global pacing of the Oxfordian CIEs.

3.3 Geological setting and stratigraphy

The LSB is an elongate basin covering large parts of northern Germany with an up to 4500 m-thick Permian-Cenozoic succession. During the Oxfordian stage, the basin was located at a paleolatitude of ~35° to 40°N within the northern hemisphere subtropical climate belt (Smith et al. 1994; van Hinsbergen et al. 2015) and covered by a shallow epicontinental sea (Ziegler, 1990) (Fig. 1). Along the southeastern margin of the basin, sedimentation was predominantly characterized by shallow-marine carbonates deposited on a homoclinal to moderately steepened epeiric ramp (Betzler et al. 2007). In the LSB, the Middle to Late Oxfordian succession is assigned to the Korallenoolith Formation (Fm.) and essentially composed of oolithic and bioclastic limestones with intercalated marls and claystones, interspersed with coral patch reefs (Helm et al. 2001).
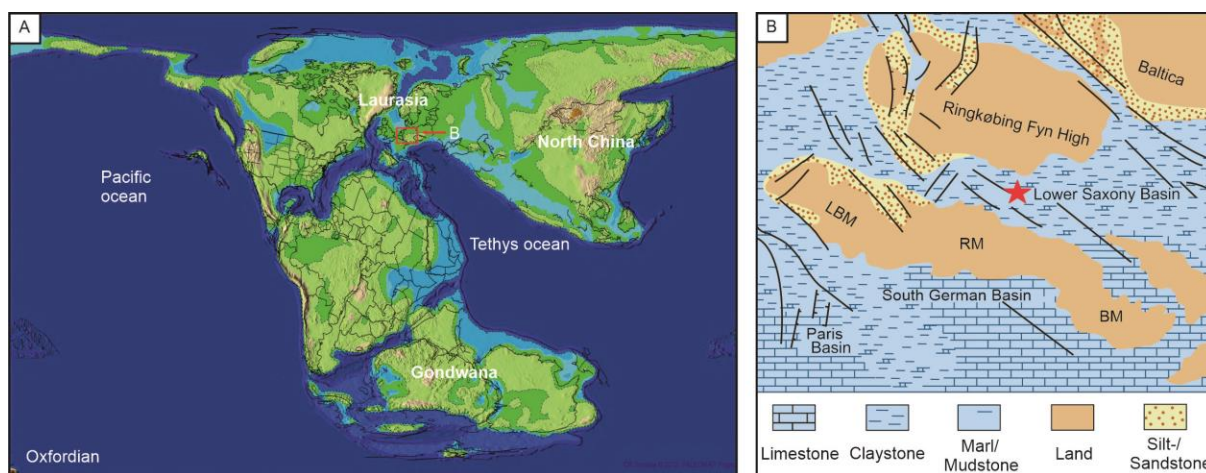
Fig. 1. (A) Global paleogeography for the Late Jurassic (~152 Ma, modified after Scotese 2014). (B) Paleogeographic reconstruction of Central Europe for the Oxfordian. Major landmasses and general marine facies distribution are shown. RM = Rhenish Massif, LBM = London-Brabant Massif; BM = Bohemian Massif. Map modified after Ziegler (1990). The approximate position of the studied outcrop in the Lower Saxony Basin is marked with a red asterisk.

Based on lithological characteristics, the Korallenoolith Fm. is further subdivided into Lower, Middle, and Upper Korallenoolith (Schulze 1975). In the Gifhorner Trough, a depression located in the eastern part of the LSB, sediment accumulation during the Late Jurassic was enhanced due to salt diapirism (Brink et al., 1992). In this area, the Korallenoolith Fm. reaches considerable thickness and contains distinct horizons of sedimentary iron ores (known as "Unteres Lager" and "Oberes Lager"), which have been mined in the subsurface until the 1970s (Berg et al. 1987).

The studied scientific Konrad #101 core was drilled in 1985 within the "management of radioactive wastes" project and is located close to the village Salzgitter-Beddingen about 500 m from the Konrad 2 mine shaft (Berg et al. 1987). Between 635.0–774.1 mbs, the core covers a ~139.1 m-thick succession of the Korallenoolith Fm (Fig. 2). The biostratigraphic framework of the Konrad #101 core is based on ostracod and foraminifera findings (Kemper 1985; Weiss 1985) and on lithostratigraphic correlation. Occurrences of age-diagnostic ostracods and foraminifera and their respective stratigraphic ranges (Gramann, 1997; Whittaker and Hart, 2009) are reported in Fig. 3. The dating of the different horizons was done by combining the stratigraphic ranges of the different specimens found together within the same horizon.

In the Konrad #101 core the Callovian/Oxfordian boundary is placed at 774.1 m, within the uppermost Ornatenton Fm "Gryphäenbank" (Fig. 2). The occurrence at 785.9 m of the ostracods *Palaeocytheridea* (*P.*) *parabakirovi* and *Lophocythere* (*L.*) *karpiskii* indicates that the uppermost Ornatenton Fm. is latest Middle Callovian in age (*Coronatum* Zone). The Middle part of the Lower Korallenoolith Fm. at 745.5 m includes the ostracod and foraminifera *Galliaecytheridea* (*G.*) *dissimilis* and *Trocholina* (*T.*) *nodulosa*, respectively, which assemblage indicates the latest Middle Oxfordian (*Pumilus* Zone). The Oxfordian/Kimmeridgian boundary is placed at 646.50 m within the Upper Korallenoolith Fm. at the first

occurrence of the ostracods *Amphicythere* (*A.*) *plena* and *Eocytheropteron* (*E.*) *decoratum*. The presence of *Paranotacythere* (*P.*) cf. *extendata* and *Macrodentina (P.) pulchra* directly below the boundary, which is in agreement with a Late Oxfordian age (*Pseudocordata* Zone) for the Upper Korallenoolith Fm.
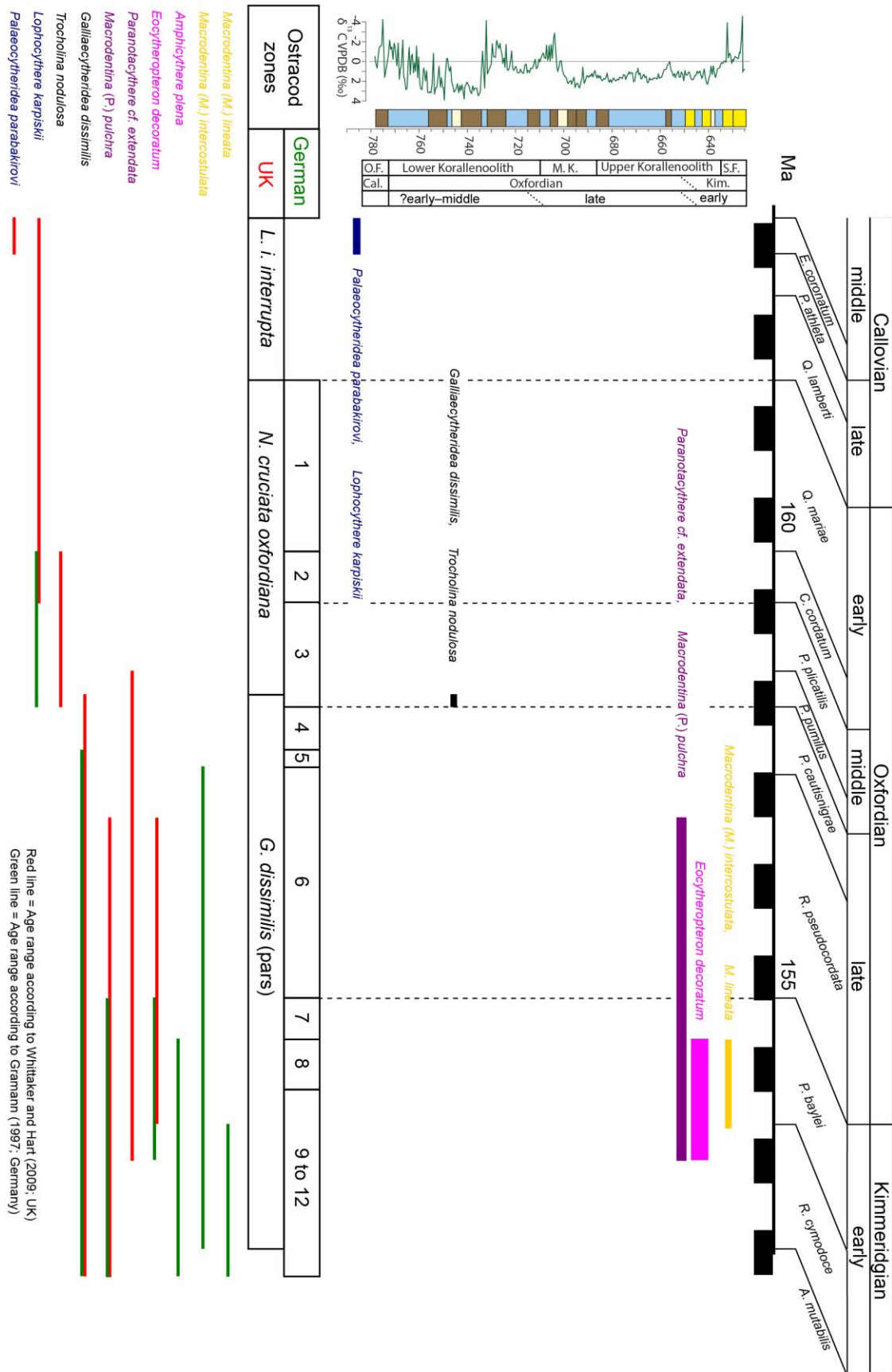
Fig. 3 Ostracod biostratigraphy of the Konrad 101 core. Range of indicative ostracod taxa is shown against stratigraphic age. Zonation schemes for northern Germany (green) and UK (red) are compared.

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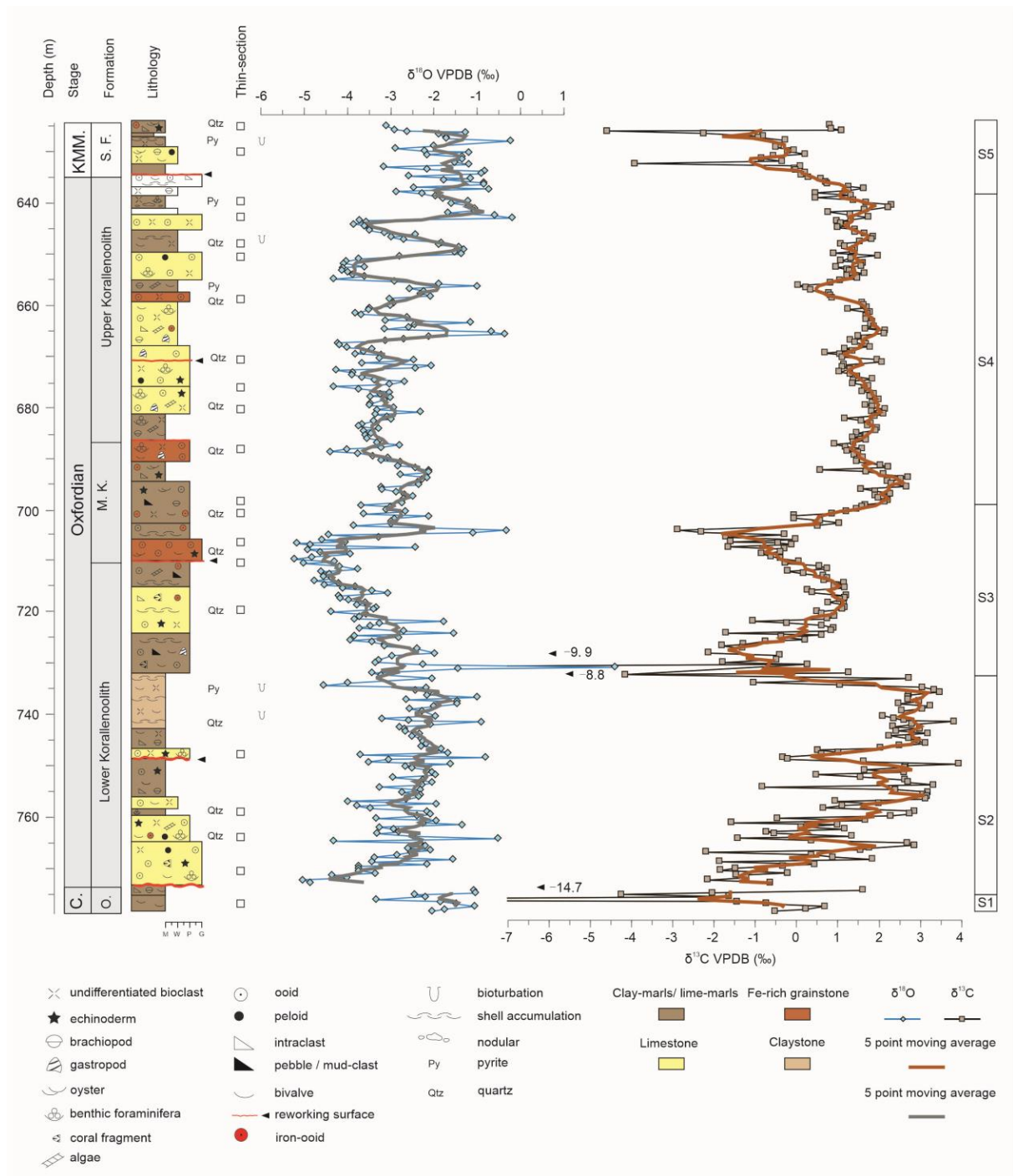
Fig. 2 Lithostratigraphy and high-resolution stable isotope stratigraphy ($\delta^{18}O$, $\delta^{13}C$) of the Konrad #101 core, Lower Saxony Basin, Germany. Stratigraphy is based on the BGR report. Intervals S1 to S5 correspond to chemostratigraphic segments of the $\delta^{13}C$ trend, where thick red line indicates a 5-point moving average. The thick gray line indicates a $\delta^{18}O$ 5-point moving average. Lithology is based on core observation and petrographic thin-section analysis. Carbonate classification follows Dunham (1962). C., Callovian; KMM., Kimmeridgian; O. Ornatenton; M.K., Middle Korallenoolith; S.F., Süntel Formation.

3.4 Methodology

The Konrad #101 core is stored at the Federal Institute for Geosciences and Natural Resources (BGR) core repository in Grubenhagen, Germany. In this study, the depth interval from 624.0 to 778.0 mbs was studied, which stratigraphically covers the uppermost Ornatenton Fm. (778.0–774.1 mbs), Korallenoolith Fm. (774.1–635.0 mbs) and lowermost Süntel Fm. (635.0–624.0 mbs). A total of 154 m was logged bed-by-bed on a dm-scale with a special emphasis on lithology, depositional texture, faunal content and sedimentary structures. A total of 350 samples were analyzed for bulk carbonate $\delta^{13}C$ and $\delta^{18}O$ isotopes (at a spacing of ~50 cm or less) at the stable isotope laboratory of the Institute of Geology, Leibniz University Hannover and 21 petrographic thin-sections were investigated. For more details on the analytical procedure, we refer to Huck, et al. (2011). For the purpose of chemostratigraphic correlation, a five-point moving average was calculated from all measured $\delta^{13}C$ values.

3.5 Results

3.5.1 Lithofacies and sediment composition

Unconformably overlying claystone of Callovian age, the Lower Korallenoolith Fm. (710.7–774.1 mbs) is composed of oolitic pack- to grainstones (Figs. 4A, B) rich in bioclastic material, which pass into clayey marls and claystones with varying sand content (Fig. 4C) and interspersed limestone beds. The upper part of the Lower Korallenoolith Fm. is made up of packstones characterized by abundant shell debris layers and an increasing abundance of Fe-rich ooids (Fig. 4D). The Middle Korallenoolith Fm. (686.9–710.7 mbs) is characterized by two distinct ironstone layers located at the bottom (706.1–710.7 mbs. "Unteres Lager", Fig. 4E) and top (686.9–691.2 mbs, "Oberes Lager") of this unit. The stratigraphic interval between the iron-rich layers is dominated by clay- and quartz-rich marls with abundant bioclastic debris and dispersed Fe-ooids. The Upper Korallenoolith Fm. (635.0–686.9 mbs) includes well-sorted oolithic pack- and grainstones (Fig. 4F) intercalating with wackestones poor in bioclasts (Fig. 4G), and interspersed beds rich in Fe-rich ooids (Fig. 4H; I). The topmost of the Korallenoolith Fm. is marked by a reworking surface, overlain by the Süntel Fm.
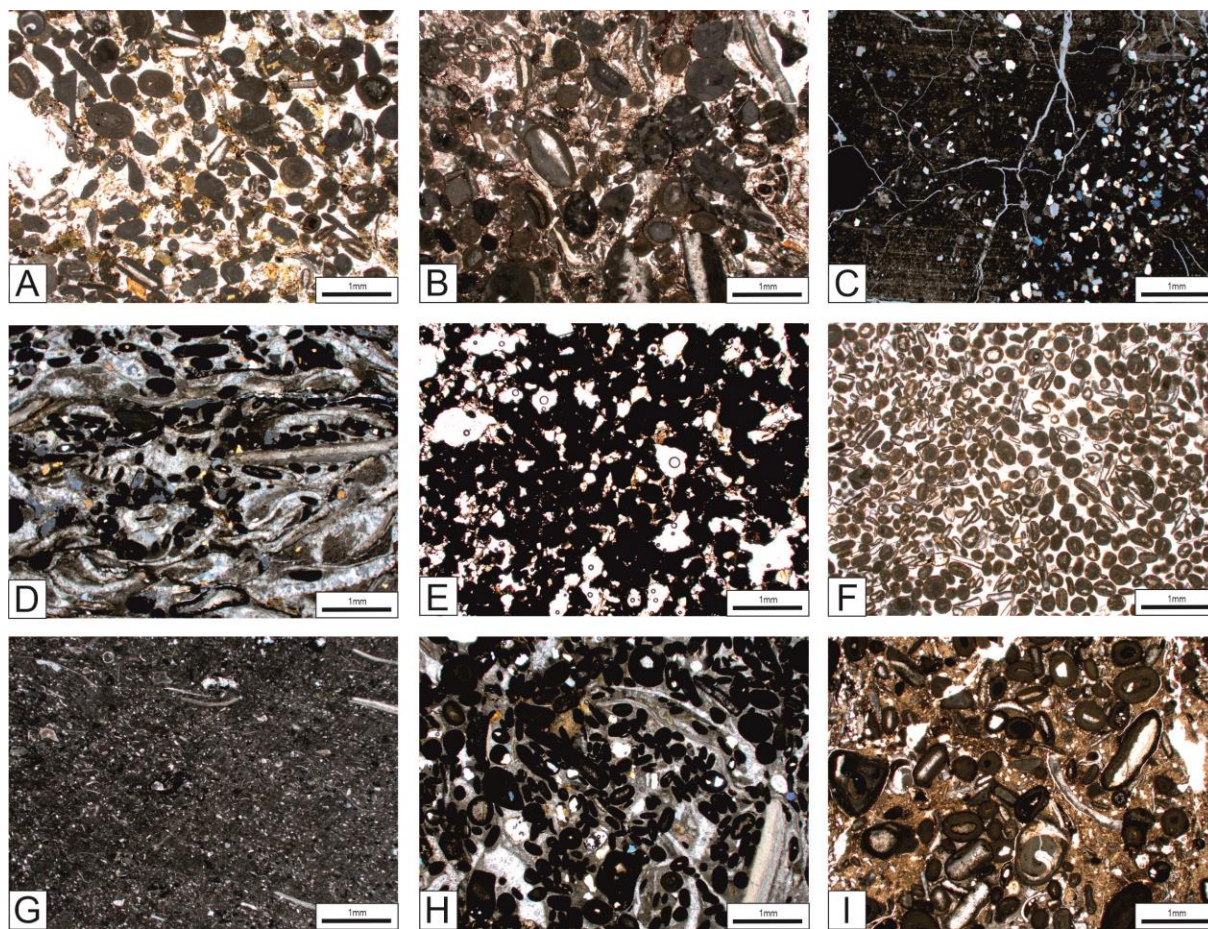
Fig. 4 Photomicrographs of characteristic carbonate microfacies associations of the Oxfordian Korallenoolith Fm. in the Konrad #101 core. (A) Loosely-packed oolitic grainstone containing large amounts of glauconite (771.0 mbs). (B) Agglutinated foraminifera-rich pack- to grainstone (763.0 mbs). (C) Argillaceous mudstone with abundant silt-sized quartz grains (759.4 mbs). (D) Bioclastic packstone showing preferred orientation and umbrella structure of bivalve shells (720.0 mbs). (E) Iron-rich oolithic grainstone of the "Unteres Lager" with individual ooids being completely replaced by iron minerals. Other components are primarily represented by well-rounded quartz grains (706.0 mbs). (F) Well-sorted oolitic grainstone with the small-sized ooids being characterized by radial fibrous calcite crystals and weak concentric banding (643.5 mbs). (G) Argillaceous mudstone comprising detrital silt-sized quartz and skeletal debris (649.0 mbs). (H) Oolithic grainstone composed of iron-rich ooids (~60-70% of the total components) (659.0 mbs). (I) Packstone composed of a mixture of iron-rich ooids and coated bioclasts, the matrix shows a mass of various sizes of skeletal material (681.0 mbs).

3.5.2 Stable isotope results

The high-resolution $\delta^{13}C$ record shows significant fluctuations through the Middle to Late Oxfordian of the Konrad #101 core (Fig. 3). Bulk $\delta^{13}C$ values vary between -4.6 ‰ and 3.9 ‰ (mean: 0.97 ‰, three outlier data were discarded: -14.7 ‰, -9.9 ‰, -8.8 ‰). Based on distinct changes of the stratigraphic $\delta^{13}C$ trend, the $\delta^{13}C$ record is divided into 5 chemostratigraphic segments. The basal segment S1 (778.0–775.8 mbs) is characterized by a sharp negative peak reaching values of -4.3 ‰. Segment S2

(775.8–732.1 mbs) displays multiple negative and positive small-amplitude excursions that are superimposed on a pronounced positive trend reaching maximum values of 3.9 ‰. A sharp negative shift in $\delta^{13}C$ values marks the onset of segment S3 (732.1–698.5 mbs), which exhibits two pronounced negative $\delta^{13}C$ excursions with amplitudes of -4.2 ‰ and -2.9 ‰, respectively. Segment S4 (698.5–637.5 mbs) starts above the $\delta^{13}C$ excursion characterizing the upper part of segment S3. Segment S4 displays a relatively constant $\delta^{13}C$ mean values of ~1.5 ‰ modulated by $\delta^{13}C$ oscillations of ~1 ‰ in amplitude. The uppermost segment S5 (637.5–624.0 mbs) shows a stepwise decrease towards more negative $\delta^{13}C$ values from a value of ~1.6 ‰ and reaching a minimum value of -4.6 ‰.

The $\delta^{18}O$ values range between -0.2 ‰ and -5.3 ‰ (mean: -2.8 ‰, one outlier data was discarded: 2.2 ‰). The $\delta^{18}O$ curve displays strong oscillations and certain parts of the $\delta^{18}O$ trend are clearly linked to lithological changes (e.g. marl-carbonate couplets). The lowermost part of the $\delta^{18}O$ curve (778.0–735.0 mbs) displays a stepwise positive trend, followed by a pronounced negative trend (735.0–705.0 mbs), reaching values of -5.2 ‰. Up-section (705.0–667.0 mbs), the $\delta^{18}O$ record fluctuates around values of ~-3 ‰. In the upper part (667.0–643.0 mbs), high-amplitude fluctuations are observed (amplitude <3.5 ‰). The uppermost part of the $\delta^{18}O$ curve (643.0–624.0 mbs) displays relatively stable values fluctuating around ~-1.5 ‰. In general, the $\delta^{18}O$ composition of the bulk rock carbonate is influenced by many factors (e.g. temperature, salinity), which can alter the original isotopic composition of the bulk rock (Mitchell et al., 1997). Hence, the $\delta^{18}O$ values will not be further discussed in this study.

3.6 Discussion

3.6.1 Significance of the $\delta^{13}C$ pattern

In order to use $\delta^{13}C$ trends for the purpose of stratigraphic correlation, potential diagenesis of the studied strata has to be assessed. Skeletal carbonate lithologies formed in shallow-marine settings are particularly prone to post-depositional alteration given their high primary porosities combined with the frequent occurrence of subaerial exposure (Immenhauser et al. 2003; Schmitt et al. 2019). The lithology of the Konrad #101 core is mainly composed of limestone, marl and claystone beds with the $\delta^{13}C$ trend showing no clear relationship with lithology across the studied core (Fig. 3). The majority of the analyzed bulk carbonate isotope values overlap with signatures obtained from well-preserved Oxfordian low-Mg shell calcite (Nunn et al. 2009; Wierzbowski 2015) and fine-grained open-marine carbonates exhibiting no signs of strong diagenetic overprint (Marshall 1992; Louis-Schmid et al. 2007). A cross-plot of $\delta^{13}C$ and $\delta^{18}O$ values reveals overall low covariance ($r^2 = 0.004$), with the individual chemostratigraphic segments showing similarly weak correlation coefficients (S1: $r^2 = 0.291$; S2: $r^2 = 0.156$; S3: $r^2 = 0.062$; S4: $r^2 = 0.004$; S5: $r^2 = 0.040$, Fig. 5). The lack of pronounced trends in C/O isotope cross-plots, which is typically caused by the addition of porosity-filling cement to skeletal carbonate (Li et al. 2006) points to the absence of strong diagenetic alteration of the Konrad #101 core stable isotope signatures. However, some pronounced short-lasting negative shifts in the $\delta^{13}C$ stratigraphic pattern are observed, which may indicate diagenetic host rock alteration by local processes. Strata directly underlying a discontinuity surface separating the Callovian Ornatenton Fm. from the overlying Korallenoolith Fm.

shows low δ¹³C values (as low as -14.7 ‰) indicative of meteoric diagenesis or remineralization of organic matter, probably associated with subaerial exposure (Marshall 1992). Another abrupt negative δ¹³C shift (segment S3, reaching values of -9.9 ‰) marks the transition from claystones to fossiliferous packstones at 732.1 mbs. The claystones and clay-rich marlstones of the Konrad #101 core contain well-preserved bioclasts, showing no re-crystallization or overgrowth. Such lithologies are usually compacted during the very early stage of diagenesis resulting in low porosity and permeability, preventing later-stage diagenetic modification (Elton et al. 2018). Despite some evidence for local diagenetic overprinting, the general trend of the bulk δ¹³C record is interpreted to reflect a primary marine signal, which can be used for chemostratigraphic correlation.
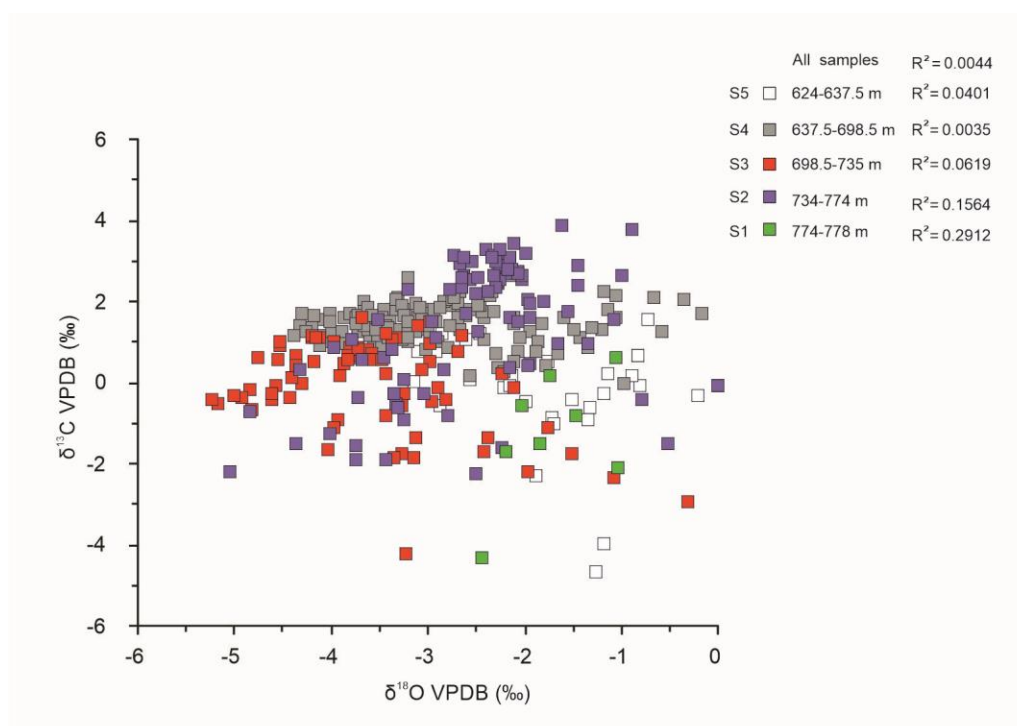
Fig. 5 Covariance plot of carbonate carbon (δ¹³C) and oxygen (δ¹⁸O) isotope values of bulk rock material derived from the Konrad #101 core. Coloring reflects groups of samples from different chemostratigraphic segments S1 to S5. Note the generally weak correlation coefficient of the analyzed stable isotope values.

3.6.2 Chemostratigraphic correlation with other Middle Oxfordian δ¹³C records

The overall pattern of the Middle Oxfordian δ¹³C record is characterized by a distinct positive CIE (MOxE) that starts at the earliest Middle Oxfordian (*Plicatilis* Zone), and reaches a maximum value (> 3.0 ‰) (*Transversarium* Zone) before being interrupted by a negative CIE within the latest Middle Oxfordian (*Transversarium* Zone). Then reaching back to the pre-excursion value during the Late Oxfordian, and shows a progressive decreasing (~1 ‰) trend toward the Oxfordian/Kimmeridgian boundary (Cramer and Jarvis 2020). Similar magnitude CIEs have been reported from marine carbonates and/or organic substrates from Europe, western Asia, and the Gulf of Mexico (Jenkyns 1996; Weissert and Mohr 1996; Padden et al. 2001, 2002; Rais et al. 2007; Louis-Schmid et al. 2007a; Martinez and Dera 2015;

O'Dogherty et al. 2018; Eltom et al. 2018; Carmeille et al. 2020; Eldrett 2022) (Fig 5). The MOxE coincides with a climatic warming trend recorded in the Paris Basin, France (Brigaud et al., 2008) and was coupled with an episode of widespread tropical carbonate sedimentation and a global spread of coral reefs (Leinfelder 2001; Helm et al. 2001; Martin-Garin et al. 2012).

In the Konrad #101 core, foraminifera and ostracod biostratigraphy enable constraining the age of the pronounced positive shift in segment S2 (Fig. 2). The foraminifera *T. nodulosa* and ostracod *G. dissimilis,* have been reported at 745.5 m within the uppermost part of segment S2. The stratigraphic ranges of *T. nodulosa* and *G. dissimilis* correspond to the C*ordatum–Pumilus* and *Pumilus–Mutabilis* sub-boreal ammonite Zones, respectively. The overlap of both biostratigraphic marker ranges indicates that the bed at 745.5 mbs is most likely *Pumilus* in age (partially equivalent to the *Transversarium* Tethyan ammonite Zone; Middle to Late Oxfordian).

A pronounced facies change at 732.1 mbs is interpreted to correspond to a regionally traceable disconformity, known as "Hauptemersionsfläche" in LSB (Klüpfel 1931; Schulze 1975), which has been assigned to the *Cautisnigrae* Zone.

The high-resolution $\delta^{13}C$ record shows a distinct positive CIE (S2 segment) in the Lower Korallenoolith Fm. followed by two negative CIEs (S3 segment)., which gives rise to a relatively stable trend in the Upper Korallenoolith Fm. This $\delta^{13}C$ trend is similar in shape and magnitude to what is characteristically observed in Middle Oxfordian carbonate carbon isotope profiles from Europe, western Asia, and the Gulf of Mexico (Fig. 6). Based on the existing microfossil biostratigraphic constraints, the positive CIE in the Lower Korallenoolith Fm. (S2 segment) is interpreted to correspond to the Middle Oxfordian MOxE, and thus can be used as an accurate stratigraphic marker within the poorly dated Korallenoolith Fm. in the LSB.
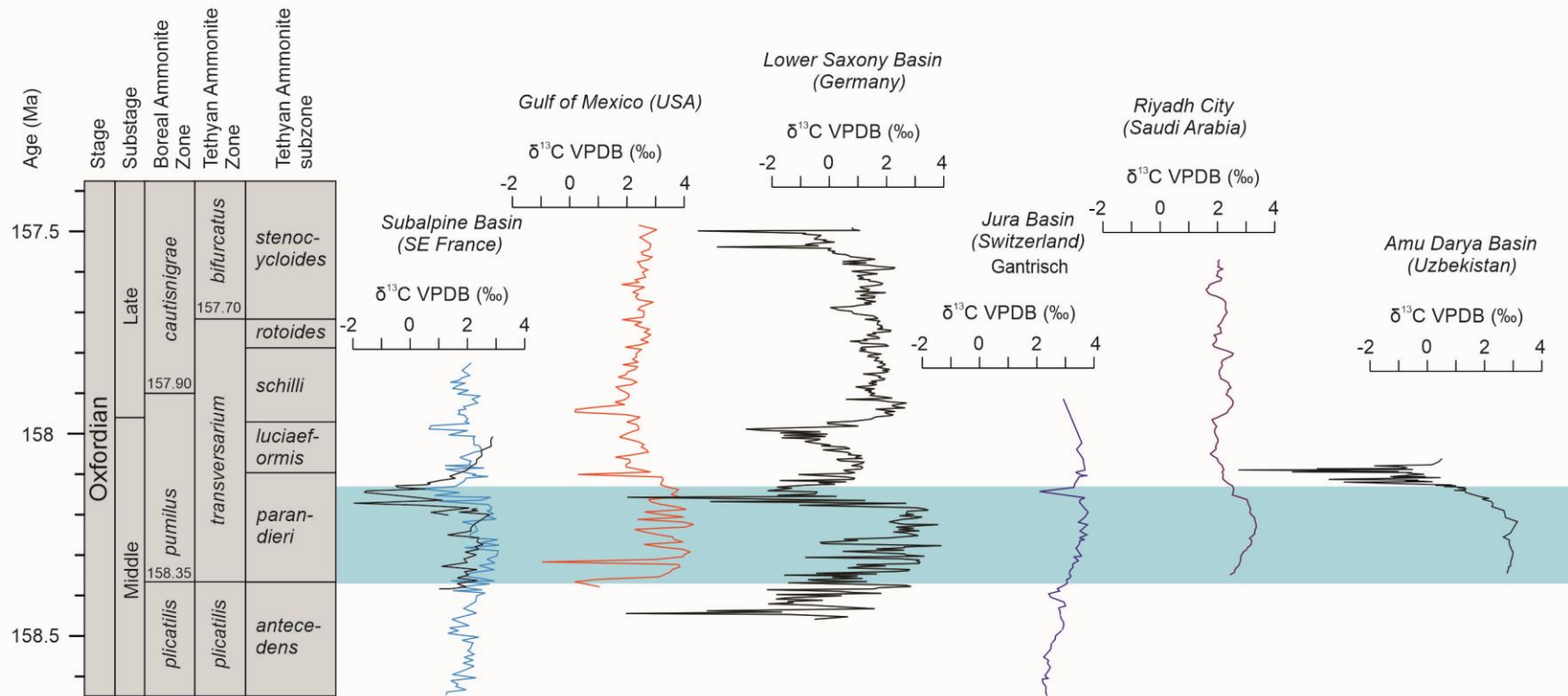
Fig. 6 Correlation panel showing a comparison of Middle to Late Oxfordian carbonate isotope records from the Lower Saxony Basin (Germany, this study) with published $\delta^{13}C$ data from the Subalpine Basin (France; Louis-Schmid et al. 2007), Gulf of Mexico (USA; Eldrett 2022), Jura Basin (Switzerland; Padden et al. 2001), Riyadh City (Saudi Arabia; Eltom et al. 2018), and Amu Darya Basin (Uzbekistan; Carmeille et al. 2020). The Blue horizontal bar corresponds to the positive carbonate CIE assigned to the lower Transversarium Zone.

3.6.3 What triggered the major Middle Oxfordian carbon-isotope excursion?

The Middle Oxfordian was a time of reef proliferation accompanied by increased organic carbon burial (Budyko et al., 1987; Weissert and Mohr 1996; Leinfelder 2001; Helm et al. 2001; Louis-Schmid et al., 2007a; Martin-Garin et al. 2012; Pearce et al. 2005; Nunn et al. 2009; Carmeille et al. 2020). The δ^{13}C pattern is characterized by a major positive shift (MOxE) observed in carbonate and organic carbon (Pearce et al. 2005; Nunn et al. 2009; Carmeille et al. 2020; Eldrett 2022). Differences in absolute values and amplitudes of the different records and substrates may be caused by local environmental effects and/or diagenesis (Husinec et al. 2022). The underlying causes for the positive MOxE are still unclear, as there is no evidence for large-scale volcanism (Rampino and Stothers, 1988; Louis-Schmid et al. 2007). In previous studies, a transgression during the Middle Oxfordian has been related to the MOxE (Jenkyns 1996; Weissert and Mohr 1996; Louis-Schmid et al., 2007a). In contrast, Pearce et al. (2005) reported that the increasing trend in δ^{13}C values corresponds to a decreasing relative sea level. However, Martinez and Dera (2015) interpreted this coincides with a maximum eccentricity of the 9 Myr orbital cycle, which altered the climatic conditions and triggered the paleoenvironmental changes. More recently, marine organic carbon burial has been put forward as a causal mechanism for the positive CIE, which coincides with a gentle second-order transgressive sea-level trend in the Middle Oxfordian (O'Dogherty et al. 2018). In turn, these paleoenvironmental changes may have been responsible for the δ^{13}C trends and excursions (Louis-Schmid et al., 2007a).

Our new high-resolution data set shows three pronounced negative CIEs. The negative CIE located at top of the S1 segment is considered to be related to a sedimentary hiatus. In the LSB the Callovian/Oxfordian transition is described as an erosional surface (Mönnig 1989; Fischer 1991). Another clear negative CIE is observed within the lowermost part of the S3 segment. This shorter-term negative excursion immediately above the positive CIE may correspond to the negative δ^{13}C excursion (~−2‰) recorded in the uppermost (*Perisphinctes*) *parandieri–luciaeformis* Tethyan ammonite subzones (partial *Transversarium* Tethyan ammonite Zone) from sections in Europe (Padden et al., 2001; Louis-Schmid et al., 2007a), Gulf of Mexico (Eldrett 2022) and western Asia (Carmeille et al., 2020). The extreme values (-8.8‰ and -9.9‰) might be related to OM remineralization processes. Padden et al. (2001) interpreted a pronounced negative δ^{13}C shift in the Oxfordian *Transversarium* Zone as the consequence of isotopically light carbon injected into the ocean-atmosphere reservoir due to the dissociation of marine methane hydrates, associated with oceanographic reorganization. The negative anomaly in the uppermost part of S3, which is mirrored in the lower ironstone layer, may represent an early-stage diagenetic modification of the carbonates (OM mineralization?). The reason behind this discrepancy of the Middle Jurassic CIE probably lies within the limited sedimentological and geochemical data available for the Oxfordian stratigraphic interval. Additional higher-resolution analysis of other geochemical proxies (e.g. $\delta^{13}C_{org}$, nitrogen isotopes, etc.) would help to disentangle between those different ideas and help to better characterize what triggered the MOxE.

3.7 Conclusions

Our δ^{13}C record is the first record of the Middle Oxfordian positive δ^{13}C excursion within the Korallenoolith Fm. in the LSB and is interpreted to reflect global δ^{13}C changes in the carbon cycle. The positive CIE observed in the Konrad #101 core is an important chemostratigraphic indicator for the inter-basinal correlation of the Lower Korallenoolith Fm. and considered to be synchronous with the globally recorded Middle Oxfordian carbon isotope excursion (MOxE). Our dataset with well-defined tie points further proves the usefulness of shallow-water isotope variations recorded in bulk carbonate as chemostratigraphic proxy. In addition, our new dataset supports the composite carbon isotope stratigraphy of the GTS 2020 compiled by Cramer and Jarvis (2020).

3.8 Acknowledgments

3.9 References

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4. $^{87}Sr/^{86}Sr$ chemostratigraphy of Oxfordian carbonate deposits, Lower Saxony Basin, Northern Germany

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4.1 Abstract

During the Oxfordian, the Lower Saxony Basin was covered by a shallow epicontinental sea, in which a thick succession of alternating marine limestones and marls was deposited. Due to the scarcity of biostratigraphic markers and numerous sedimentary gaps, the stratigraphic dating is still uncertain and hampers further studies on a basin-wide scale. Chemostratigraphy represents a reliable means of contrasting and calibrating biostratigraphic schemes on local and global scales. New biocalcite-derived $^{87}Sr/^{86}Sr$ data for 11 well-preserved shells and shell fragments from the Oxfordian Korallenoolith Fm. of Lower Saxony Basin are used to identify secular trends in seawater and to constrain the depositional age of the Korallenoolith Formation. Unfortunately, the analyzed data deviate significantly from the Oxfordian open marine Sr-isotope signature and fail to provide a more precise age assignment. We discuss possible environmental factors that may have affected the $^{87}Sr/^{86}Sr$ ratios derived from shell material of the Korallenoolith Fm. The new findings indicate that continental freshwater discharge was the most likely controlling factor for the observed seawater $^{87}Sr/^{86}Sr$.

Keywords: Shell Geochemistry, Oxfordian, Strontium stable isotope, Boreal realm, Late Jurassic

4.2 Introduction

During the Oxfordian stage (Late Jurassic; 161.5–154.8 Myrs), the Lower Saxony Basin (LSB) was covered by a shallow epicontinental sea, which facilitated the accumulation of carbonate-rich sediments (Ziegler, 1990). These shallow-marine deposits are composed of alternating limestones, marls, and coral reef-bearing horizons and correspond to the Korallenoolith Formation (Fm.). Despite multiple biostratigraphic schemes that have been constructed, the stratigraphy and subdivision of the Upper Jurassic rocks of the LSB are still poorly defined. The shallow-marine carbonates of the Korallenoolith Fm. probably formed under varying salinity regimes that lack typical marine index fossils. Due to the scarcity of biostratigraphic markers and numerous sedimentary gaps, the stratigraphic dating is still uncertain and hampers further studies on a basin-wide scale. As ammonites are scarce or lacking, other biostratigraphic schemes have been developed, including ostracods, benthic foraminifera, charophytes, terrestrial and marine palynomorphs, and vertebrate remains (Schudack, 1994; Weiß, 1995; Gramann et al., 1997; Mudroch et al., 1999; Luppold, 2003). However, most of those organism groups are endemic due to the restricted palaeogeographic position of the LSB, which had limited exchange with the open ocean. Given this poor dating, a correlation on supra-regional and/or global scales remains ambiguous and imprecise (Jach et al., 2014; Zuo, 2017). As a result, a stratigraphic age assignment of the Korallenoolith Fm. in the LSB remains difficult, although some excellent and undeformed Upper Jurassic sections are exposed in the LSB, including the Bisperode section (Ith syncline).

At any given time, Strontium has a long ocean residence time of ~2.4*10^6 years (Jones and Jenkyns 2001) and can be viewed as a global signal, with its isotopic composition reflecting the relative inputs of Sr from rivers (continental flux with high, radiogenic $^{87}Sr/^{86}Sr$ ratios) and from submarine hydrothermal systems (mantle flux with relatively low $^{87}Sr/^{86}Sr$ ratios) (Faure, 1986; Bruhn and Veizer, 2005). Secular variations of the $^{87}Sr/^{86}Sr$ ratio are used as a tool for strontium isotope stratigraphy (SIS), which represents a reliable means of contrasting and calibrating the divergent biostratigraphic schemes on local and global scales (McArthur et al., 2001, 2012, 2020; Jenkyns et al., 2002, Huck et al., 2013; Frijia et al., 2015). Low-Mg calcite shells are considered an ideal geochemical archive for capturing contemporaneous seawater $^{87}Sr/^{86}Sr$ ratios due to their resistance to diagenesis (Popp et al., 1986; Brand et al., 2011; Huck et al. 2011). Previous studies have demonstrated that low-Mg calcite shells are a valuable tool for age assignment of shallow marine strata (Schneider et al. 2009, Heimhofer et al. 2012, Horikx et al. 2014; Zuo et al. 2018; Schmitt et al. 2020). Most existing SIS studies dealing with the Oxfordian interval focus on pelagic and hemipelagic deposits whereas data from shallow-water carbonates is comparatively rare. Overall, only a limited amount of SIS data is available for the Oxfordian (Wierzbowski et al., 2017; McArthur et al., 2020). In addition, crucial Sr isotope data is still lacking for the Oxfordian–Kimmeridgian transition, and for some other intervals of the Middle-Upper Jurassic, which makes the precise determination of seawater strontium isotope ratios during these periods difficult (Wierzbowski et al. 2017). Within the LSB, Zuo et al. (2018) used SIS to establish a refined stratigraphic framework for the Kimmeridgian Süntel Fm. Although Bruhn et al. (2005) presented $^{87}Sr/^{86}Sr$ ratios from bulk rock samples from the Oxfordian Korallenoolith Fm., precise dating and correlation for Oxfordian strata within the LSB based on pristine shell material are still lacking.

The aim of this study is to develop a composite Sr-isotope stratigraphic record for the Oxfordian limestone successions in the LSB. From the Bisperode section and the Konrad #101 core, well-described high-resolution lithological logs with detailed sedimentological information of the Korallenoolith Fm. have been built (Betzler et al. 2007; Cäsar 2012; Zuo, et al. 2017; Zhang et al. 2023). We combine morphological preservation, CL characteristics, and trace elements threshold values to assess the preservation of fossil shell material, which is subsequently analyzed for $^{87}Sr/^{86}Sr$ ratios. The new Sr-isotope data from the Oxfordian part of the Bisperode section and Konrad #101 core will be compared with previously published $^{87}Sr/^{86}Sr$ records (Wierzbowski et al., 2017; McArthur et al., 2020). Based on these new results, the existing stratigraphic age assignment of the Korallenoolith Fm. in the LSB will be critically assessed. Finally, a supra-regional stratigraphic correlation with other successions in the peri-Tethyan and western Tethyan domains can be proposed.

4.3 Geological setting

The LSB, located on the southern margin of the Central European Basin, is one of several rift- and wrench-induced "marginal troughs", that formed a series of E-W trending horst-and-graben structures (Betz et al., 1987; Ziegler 1990; Senglaub et al., 2006). With a length of ~300 km and a width of ~65 km, the LSB formed an elongate, E-W trending basin bordered by the Rhenish Massif to the South and the Ringkøbing-Fyn High to the North (Fig. 1). The LSB contains a maximum sedimentary thickness of ~4500 m (Betz et al. 1987; Mazur et al. 2005; Kästner et al., 2010). Stratigraphic sections located on the uplifted horst areas may show less stratigraphic thickness and contain fewer small- and medium-scale cycles compared to the adjacent graben areas (Kästner et al. 2008). During the Oxfordian, the LSB was located at a palaeolatitude of about ~ 35°N (van Hinsbergen et al. 2015) and can be viewed as a tributary sea of the Tethys, which resulted in the interchange of fauna and flora between the Boreal and the Tethyan Realms (Helm et al. 2001; Cäsar, 2012). In the LSB, the middle to late Oxfordian succession is assigned to the Korallenoolith Fm., which belongs to the NW German Malm Group (Helm et al. 2003). The Korallenoolith Fm. consists of reef-bearing oolithic limestones, which were formed within a shallow-marine subtropical environment with limited terrestrial influx. Deposition took place on a homoclinal carbonate ramp setting (Helm et al. 2003; Betzler et al. 2007; Kästner et al. 2008; Cäsar 2012; Zuo et al. 2017; Zhang et al. 2023).
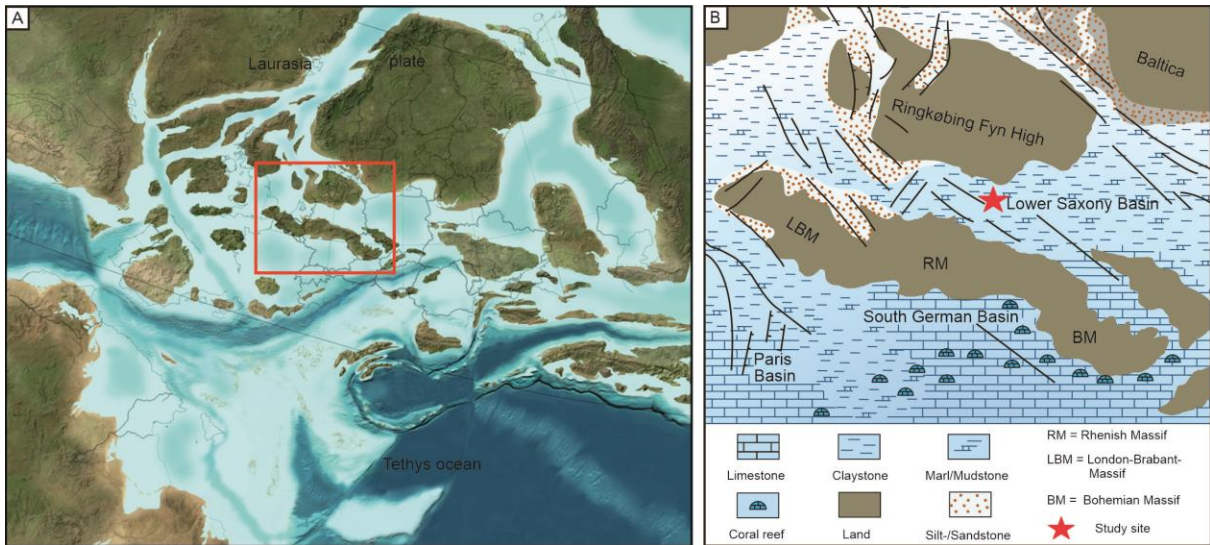
Fig. 1. (A) Paleogeographic maps of Europe and adjacent regions for the Late Jurassic (150 Ma, modified after Blakey, 2011). (B) Paleogeographic reconstruction of Central Europe for the Oxfordian. Major landmasses and general marine facies distribution are shown. The approximate position of the studied outcrop in the Lower Saxony Basin is marked with a red asterisk.

The studied sites are situated in northern Germany (Fig. 2). and include an abandoned quarry (Bisperode section) located ~2 km southwest of the village Lauenstein and a scientific drill core (Konrad #101 core) located close to the village Salzgitter-Beddingen about 500 m of the Konrad 2 mine shaft (Berg et al. 1987). The lithology is essentially composed of oolithic and bioclastic limestones with intercalated marls and claystone, interspersed with coral patch reefs in the Bisperode section. More detailed information on the sedimentary facies and depositional settings encountered in the Bisperode section and the Konrad #101 core can be found in chapters 2 and 3.
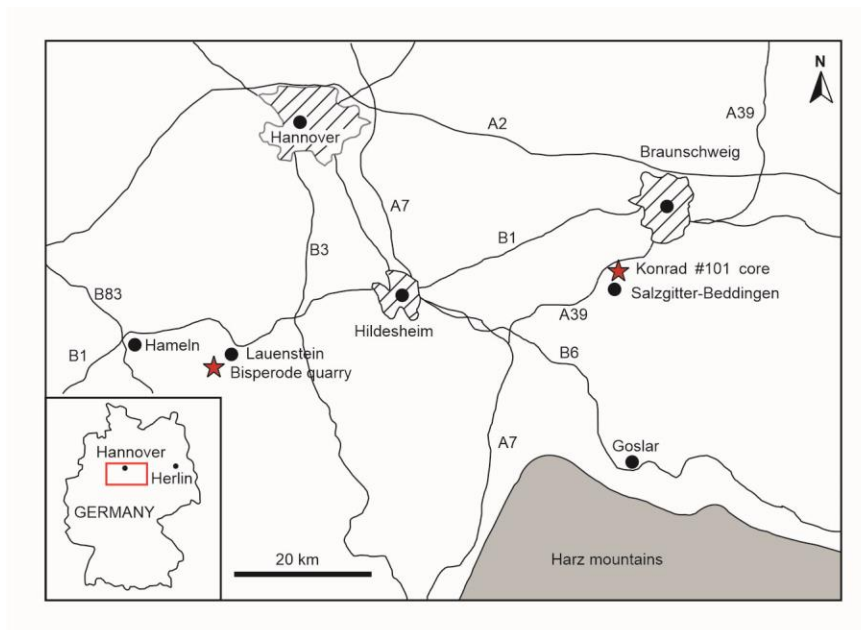

Fig. 2. Location of the studied sites in northeast Niedersachsen, Germany, The Bisperode quarry and Konrad #101 core location are marked with asterisks.

4.4 Materials and methods

4.4.1 Materials

A total of 30 shells were collected for SIS from the Bisperode section and an additional 16 shell fragments were obtained from the Konrad #101 core, respectively. The shells and shell fragments from the Bisperode section are mainly derived from brachiopods, oysters, *trichites* bivalves (a group related to *Pinnidae*), and rarely from echinoderms. Brachiopods are represented by *Zeilleriidae* and *Loboidothyrididae*, which both belong to the *Terebratulida* order (Gervais, 1987; Fischer, 1991). The shell fragments from the Konrad #101 core are very small (< 10 mm) and do not allow identification on a taxonomic level. In consequence, all samples from the Konrad #101 core are grouped simply as shell fragments without further differentiation.

Given the potential alteration of primary shell calcite during early and later-stage diagenesis, it is necessary to use multiple methods (visual inspection, petrographic thin-section and cathodoluminescent microscopy, and trace element geochemistry) to assess the preservation state of the studied shells used for seawater $^{87}Sr/^{86}Sr$ reconstruction (Brand et al., 2012a; Korte et al. 2006; McArthur et al., 2012; Immenhauser et al., 2016; Wang et al., 2018).

4.4.2 Petrography and cathodoluminescence analyses of shell material

Before further processing, all of the sampled shells have been visually inspected to avoid bio-eroded parts, cement infills, and other impurities. Subsequently, the shells were thin-sectioned in order to analyze the internal shell structure, using an Olympus BX53 microscope equipped with an Olympus SC50 camera, at Institute for Geology, Leibniz University Hannover. In addition, cathodoluminescence (CL) microscopy was carried out at Aarhus University using a cold cathodoluminescence (Nuclide ELM2) operating at 12 kV with a beam current of 3 mA. Exposure to the electronic beam (before taking the photo) was limited to 15~30 seconds. Photographic exposure time was set to 2-4 s and to be uniform for consistency.

Visible growth increments, compact fibrous microstructure and negligible impact of bioerosion and fracturing are considered morphological criteria indicative of well-preserved mollusc shell material (Schmitt et al. 2020, 2022). Following Garbelli et al. (2019), the luminescence characteristics of the shells were classified as non-luminescent (NL), slightly luminescent (SL), and bright luminescent (L). Non-luminescent shells showing rare bright microfractures are assigned to the first category (NL), but if the fissures occur more frequently, the samples are categorized as SL. Only the most pristine shells (showing visible growth increments and compact fibrous microstructure of the outer shell layer, and predominantly non-luminescent shell areas) were selected for further geochemical analysis.

4.4.3. Elemental and strontium-isotope analyses

Following the strict petrographic screening, 23 shell samples from Bisperode (7 oysters, 4 brachiopods, 9 *trichites* bivalves, and 1 echinoderm fragment), and 14 shell fragments from the Konrad #101 core

were selected for subsequent trace element measurement (Table 1). For major and trace element analyses, several milligrams (~10) of powder were micro-drilled from different positions of each shell. The powders were analyzed for Ca, Mg, Mn, Fe, and Sr in order to assess the potential diagenetic alteration of the low-Mg shell material. Analyses were performed using inductively coupled plasma-atomic emission spectrometry (ICP-AES) at the isotope laboratory of the Institute of Geology, Mineralogy and Geophysics at the Ruhr-University Bochum, Germany. For more details on the analytical procedure compare Huck et al. (2011).

Based on the petrographic and element geochemical results, 11 well-preserved shells and shell fragments were selected for analysis of $^{87}Sr/^{86}Sr$ ratios at the Ruhr-University Bochum, Germany, using a thermal ionization mass spectrometer (Finnigan MAT 262) in dynamic mode. For more details on the analytical procedure, please refer to Huck et al. (2011). In order to be consistent with the normalization used for the compilation of the SIS reference curve of McArthur et al. (1997), the $^{87}Sr/^{86}Sr$ ratios of the samples were adjusted to a value of 0.709175 for the USGS EN-1 standard.

Table 1. Analytical results (Sr-isotope and trace elements) of low-Mg calcite shells from Bisperode sections and Konrad #101 core

Locality	Fossils	Height(m)	Sample No.	Mg	Sr	Fe	Mn	87Sr/86Sr	87Sr/86Sr
					(ppm)				
Bisperode	brachiopod	44	SB7.7	2697	606	69	16	0.706954	5
	brachiopod	45	SB8.5-B	1785	576	221	19	0.706913	5
	brachiopod	45	SB8.5-D	1689	563	98	12	-	-
	brachiopod	24.5	LPb-3	1811	458	698	31	-	-
	trichites	45	SB8.5-A	5705	170	488	106	-	-
	trichites	61.5	SB25.2	4173	706	220	35	0.706909	5
	trichites	94	SB57.2	1469	631	115	7	-	-
	trichites	95	SB58.5	3688	433	1324	75	-	-
	trichites	101.5	SB65-A	4025	290	109	57	-	-
	trichites	101.5	SB65-B	3816	192	273	77	-	-
	trichites	101.5	SB65-C	3702	197	337	73	-	-
	trichites	119	D82.5-A	6266	632	3945	71	-	-
	trichites	119	D82.5-B	5237	685	259	29	0.706914	5
	oyster	10	DY10	1400	551	301	23	-	-
	oyster	12.15	DY11.5	745	623	336	13	0.706887	5
	oyster	97	SB60.5-A	2064	470	196	21	-	-
	oyster	97	SB60.5-B	1077	617	90	9	0.706923	5
	oyster	28	LPb-6.5A	814	574	565	64	-	-
	oyster	28	LPb-6.5B	2186	588	222	24	-	-
	oyster	30	LPb-8.5A	708	532	321	34	-	-
	oyster	30	LPb-8.5B	1209	610	279	29	0.706914	5
	oyster	30	LPb-8.5C	6207	53	1620	104	-	-
	echinoderm	45	SB8.5-C	3937	105	283	48	-	-
Konrad	shell	649.5	K649.5A	1905	688	2141	102	0.706981	5
	shell	649.5	K649.5B	3501	853	6155	150	0.707193	5
	shell	655.79	K655.79A	3889	312	26463	398	-	-
	shell	655.79	K655.79B	2913	485	12874	259	-	-
	shell	748.2	K748.2	1386	983	4387	409	0.706950	5
	shell	753.5	K753.5	740	620	3442	275	0.706966	5
	shell	766.48	K766.48	268	550	254	57	-	-
	shell	776.7	K776.7	382	505	1387	60	-	-
	shell	777.45	K777.45	3842	598	10662	150	-	-
	shell	777.7	K777.7	452	517	597	70	-	-
	shell	778.40A	K778.40	642	522	682	77	-	-
	shell	778.40B	K778.40	513	507	5105	79	-	-

4.5 Results and interpretation

4.5.1 Shell microstructure and cathodoluminescence characteristics

Under the petrographic microscope, most of the brachiopod and oyster shell specimens show detailed prismatic layers and growth lines, with a clearly visible alternation of light to dark lamellae, indicating good preservation (Fig. 3). Examples include oyster shells exhibiting near-horizontally foliated orientations of prismatic layers (specimen DY11.5, Fig. 3A). Stacked growth bundles with different orientations are clearly visible in a shell fragment of questionable brachiopod origin (specimen K735.5, Fig. 3B). Two types of foliated wall structures with different foliation orientation are observed in a shell fragment of uncertain taxonomic assignment (specimen K753.5, Fig. 3C). Well-preserved brachiopod shells are characterized by a parallel fibrous wall structure oriented at a low angle to the shell margin (specimen SB 8.5B, Fig. 3D) and by a well developed foliated structure (specimen SB7.7, Fig. 3E). In contrast, *trichites* shells show a prismatic shell structure composed of coarse and well-developed calcite prisms, well visible under cross-polarized light (specimen D 82.2, Fig. 3F). The coarseness and inclusion-rich nature of the calcite prisms may indicate that the shell has undergone some diagenetic modification.

Most of the analyzed specimens (brachiopods, oysters) remain non-luminescent in most parts of the shell. Comparison of CL and transmitted-light microscopy illustrates well the non-luminescent (NL) character of well-preserved brachiopod shells, which contrast with the strongly luminescent, fine-grained matrix (Fig. 4A, B). Here, only rare luminescent fissures occur, which correspond to growth lines (Fig. 4C, D). The visually well-preserved *trichites* shells document often different levels of luminescence. Several samples show significant luminescence variability within the shell, including parts being slightly luminescent (SL) (Fig. 5A). Here, luminescence occurs between individual calcite prisms (Fig. 5B). In other parts of the shells, more prevalent bright luminescence (L) indicates diagenetic alteration due to cement infill (Fig. 5C). In contrast, strongly diagenetically altered *trichites* shells show bright luminescence (L) encompassing the entire shell (Fig. 6A) and uncovering the individual growth bands (Fig. 6B, C).
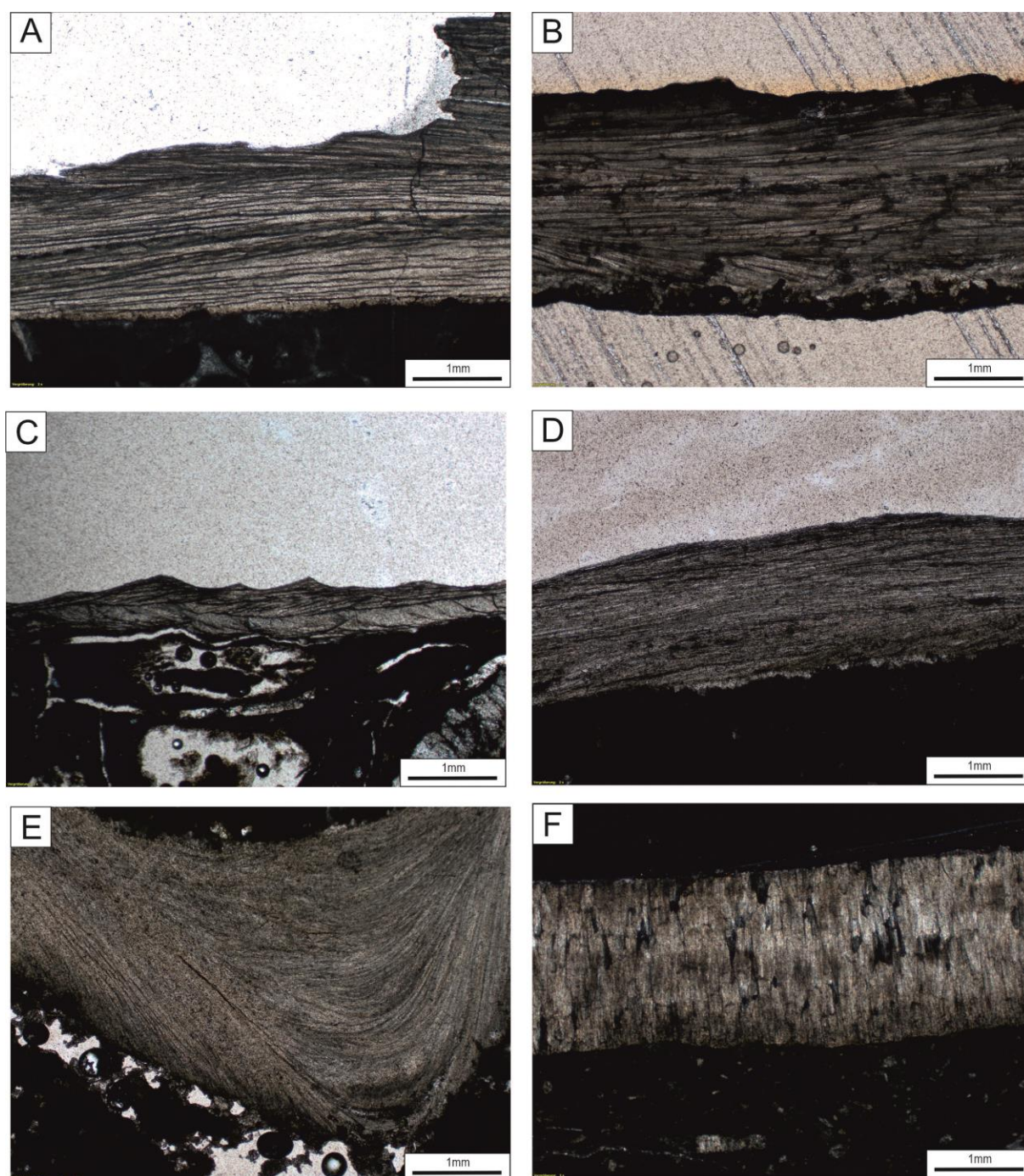
Fig. 3. Petrographic thin-section photomicrographs of selected brachiopod, oyster, and trichites shells from Bisperode quarry section and Konrad #101 core. (A) Specimen DY11.5 shows an oyster shell composed of individual calcite layers with near-horizontally foliated orientation. (B) Specimen K735.5 is tentatively assigned to represent a brachiopod shell fragment showing stacked calcitic bundles with different orientations. (C) Specimen K753.5 is tentatively assigned to represent a brachiopod shell fragment showing two types of foliated wall structure. The two layers exhibit different foliation orientations. (D) Specimen SB 8.5B represents a brachiopod shell with a well-developed parallel fibrous wall structure oriented at a low angle to the shell margin. (E) Specimen SB7.7 provides a detailed view of the foliated structure of a brachiopod shell. (F) Specimen D 82.2 shows a trichites shell under cross-polarized light with its characteristic coarsely prismatic structure.

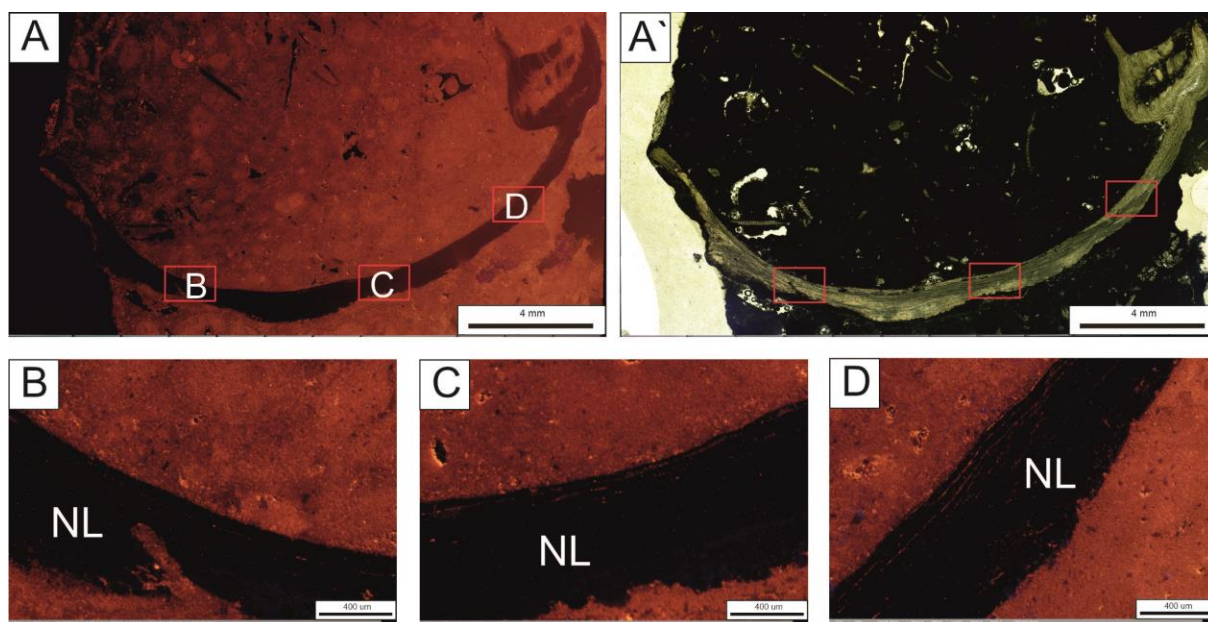Fig. 4. Detailed view of brachiopod specimen SB8.5-B (Bisperode section) under CL (A) and transmitted light (A'). Enlargements of selected shell areas are marked by the red boxes labeled B, C, D. (B) Non-luminescent (NL) shell area with a bioerosion structure permeated by luminescent diagenetic cement. (C, D) Non-luminescent (NL) areas show thin luminescent fissures on the inner side of the shell parallel to growth lines.
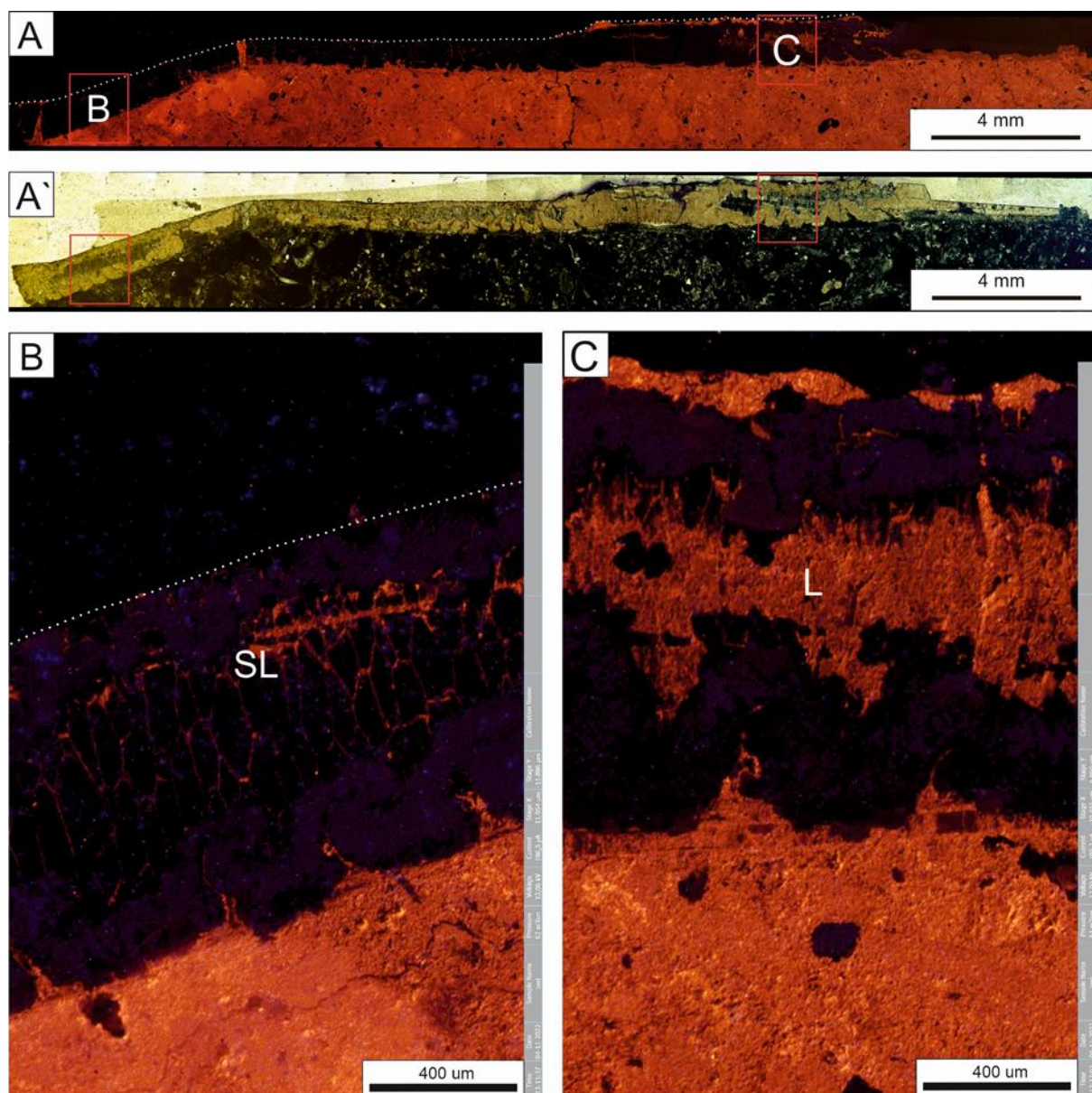
Fig. 5. Detailed view of trichites specimen SB25.2 (Bisperode section) under CL (A) and transmitted light (A') illustrating different levels of preservation. Enlargements of selected shell areas are marked by the red boxes labeled B, C. (B) Coarsely prismatic shell structure showing luminescent boundaries between individual calcite prisms. (C) Shell area showing widespread bright luminescence (L) indicating cementation/recrystallization during diagenesis.
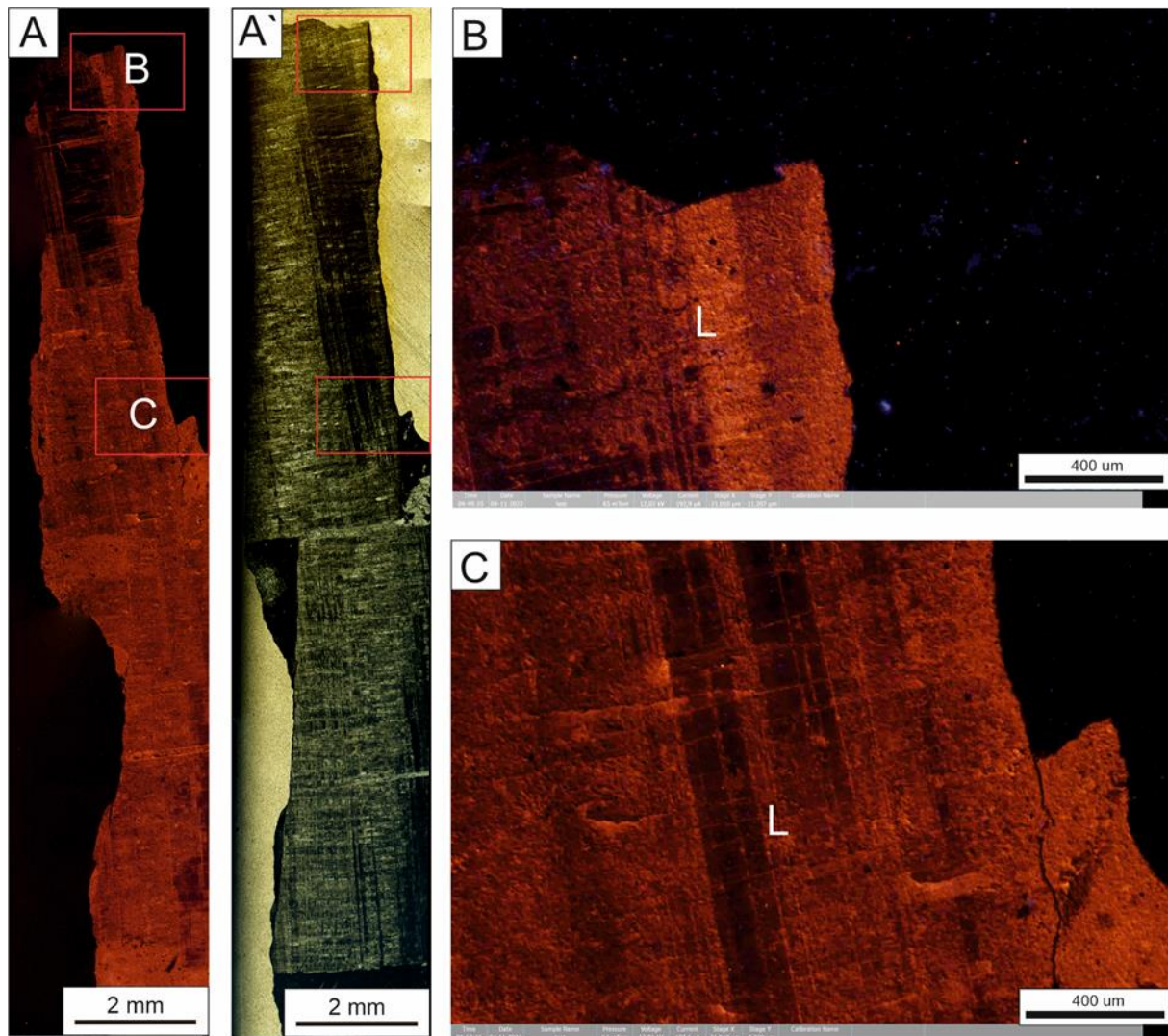
Fig. 6. Detailed view of trichites specimen SB 65 (Bisperode section) under CL (A) and transmitted light (A') showing strong luminescence (L) across the entire shell. Enlargements of selected shell areas are marked by the red boxes labeled B, C. (B, C) Bright luminescence covering the entire trichites shell indicates strong diagenetic alteration and loss of the primary geochemical information.

4.5.2 Element concentrations and isotopic compositions

The oyster shell samples from Bisperode show the following ranges of major and trace element contents. Mn varies between 9 and 104 ppm (n=9), Fe between 90 and 1.620 ppm, Sr between 53 and 623 ppm, and Mg between 708 and 6.207 ppm. Brachiopod shell material from Bisperode (n=4) shows variations of Mn between 12 and 31 ppm, Fe between 69 and 698 ppm, Sr between 458 and 606 ppm, and Mg between 1.689 and 2.697 ppm. *Trichites* shell specimens from Bisperode (n=9) exhibit Mn concentrations between 7 and 106 ppm, Fe between 109 and 3945 ppm, Sr between 170 and 706 ppm, and Mg between 1.469 and 6.266 ppm. For a single echinoderm fragment, concentrations are Mn 48 ppm, Fe 283 ppm, Sr 105 ppm, and Mg 3.927 ppm. The different shells fragments (n=14) obtained from the Konrad #101 core show concentrations of Mn between 57 and 409 ppm, Fe between 57 and 26.463

ppm, Sr between 312 and 983 ppm, and Mg between 268 and 3.889 ppm. All major and trace element results are shown in Table 1.

Only shell samples showing element concentrations below the defined cut-off values (discussed in section 5.1) were analyzed for their $^{87}Sr/^{86}Sr$ ratios (Table 1). The Sr-isotope ratios obtained from different types of shells located in the same or adjacent stratigraphic horizons show very similar values ranging between $1*10^{-6}$ and $9*10^{-6}$ (Zuo 2018). Sr-isotope values (n=7) from the Bisperode quarry section vary between $0.706887 ± 5*10^{-6}$ to $0.706954 ± 5*10^{-6}$, which is generally within the range of values reported for Late Jurassic sea water (McArthur et al., 2020). Besides, 4 Sr-isotope values ($0.706950 ± 5*10^{-6}$ to $0.707193 ± 5*10^{-6}$) from the Konrad #101 core have been obtained. One value ($0.707193 ± 5*10^{-6}$) is highly radiogenic compared to Late Jurassic global seawater proxy (McArthur et al. 2020) and this data was excluded from further interpretation. Three of the values fall within the Sr isotope range reported for Late Jurassic seawater (Rais 2007; Wierzbowski et al. 2017; McArthur et al. 2020), but more radiogenic compared to the values from the Oxfordian. This data will be discussed further in 5.1.

4.6 Discussion

4.6.1 Preservation of shells and reliability of strontium-isotope ratios

Only marine precipitates that have retained the original Sr-isotope ratio of the ocean will give correct SIS ages (Frijia et al., 2015). Oysters mineralize a primarily low-Mg-calcitic shell usually comprised of prismatic and foliate layers (Carter 1990). The specific mineralogy makes them less prone to diagenetic processes, which potentially can alter the primary chemical composition of the shell material (Schneider et al. 2009, Heimhofer et al. 2012, Horikx et al. 2014). Modern brachiopod shells show little taxonomic or vital effects on their $^{87}Sr/^{86}Sr$ composition (e.g., El Meknassi et al., 2018; Immenhauser et al., 2016; Zaky et al., 2019) and previous studies have considered brachiopod shells to be one of the best archives for capturing the Sr-isotopic signature of ancient ocean waters due to their resistance to diagenesis (Brand et al., 2011; Popp et al., 1986; Wang et al. 2020). *Trichites* shells represent a novel substrate for chemostratigraphic applications, and geochemical information on shell composition is essentially lacking (Brigaud et al., 2009, Zuo et al. 2018). *Trichites* and oyster shells that have been recovered from the same stratigraphic levels display similar Sr-isotope values (Brigaud et al. 2009). Zuo et al. (2018) reported *trichites* shells showing elemental contents comparable with brachiopod and oyster low-Mg calcite. These studies suggest the absence of strong vital effects and indicate a rather limited diagenetic overprint for the investigated *trichites* shells (Brigaud et al., 2009, Zuo et al. 2018). In summary, all the collected shells (oyster, brachiopod, and *trichites*) can potentially be used as archives for ancient seawater $^{87}Sr/^{86}Sr$ reconstruction. However, diagenesis may have influenced the primary $^{87}Sr/^{86}Sr$ signal of the shell, so it is fundamental to evaluate the preservation state of materials used for seawater $^{87}Sr/^{86}Sr$ reconstruction (Brand et al., 2012a; Korte et al., 2006; McArthur et al., 2012; Immenhauser et al., 2016; Wang et al., 2018, 2021). Shell samples are considered well-preserved when their shell structure shows good preservation under the petrographic microscope and absence of luminescence

under CL (Horikx et al. 2014; Zuo et al. 2018; Wang et al., 2018, 2021). In addition, the trace element concentrations of shell calcite are widely used to further distinguish the preservation state of shells.

The degree of diagenetic alteration of primary shell calcite of carbonate-secreting organisms is verified by using Sr, Fe, and Mn abundances (Brand and Veizer 1980, Al-Aasm and Veizer 1986, Veizer et al. 1999, Huck et al. 2011, Horikx et al. 2014). High Mn and Fe concentrations in skeletal calcite are considered to indicate recrystallization in a reducing environment, involving the partial or complete equilibration of the Sr-isotope ratio with that of the diagenetic fluid, also resulting in low Sr concentrations (Al-Aasm and Veizer, 1986). Brand et al. (2011) suggested dynamic limits for trace elemental concentrations to differentiate preserved and altered shell materials. For low-Mg brachiopod calcite shells precipitated from normal marine waters, Mn values of < 100 ppm and Sr values > 600 ppm have been proposed as cut-off values, reflecting insignificant diagenetic overprint (van Geldern et al., 2006; Wierzbowski, 2015). In this study, well-preserved brachiopod samples are defined in comparison to typical threshold elemental values used by other authors (e.g., van Geldern et al., 2006; Wierzbowski, 2015) with a single exception. Sample SB8.5-B is considered as well preserved despite a Sr content (576 ppm) slightly below the threshold value. For Fe concentrations, we follow Zuo et al. (2018), who proposed values of < 700 ppm for brachiopod calcite obtained from the LSB, which is higher than the typical threshold values used by other authors (e.g., van Geldern et al., 2006; Wierzbowski, 2015). For oyster shell calcite, Schneider et al. (2009) analyzed Late Jurassic oysters in the Lusitanian Basin and proposed threshold values < 100 ppm for Mn and < 700 ppm for Fe. For Sr concentrations, Zuo et al. (2018) suggested threshold values > 600 for samples derived from the LSB based on a comparison with Schneider et al. (2009). In the present study, we follow the proposed values (Mn < 100 ppm, Fe < 700 ppm, Sr > 600 ppm) for oyster shell calcite considered to reflect insignificant diagenetic overprint (Fig. 7). *Trichites* shell material represents a novel substrate for chemostratigraphic applications, and geochemical information on shell composition is rare. Here we follow the cut-off values proposed by Zuo et al. (2018), which are Mn < 100 ppm, Fe < 700 ppm, and Sr > 600 ppm. Sample SB 57.2 is discarded as it only contains 7 ppm Mn. Echinoderm biocalcite is discarded as the original porous stereome is typically filled with diagenetic cement resulting in alteration of its primary geochemical composition. Based on their shell microstructure, the small shell fragments from the Konrad #101 core are tentatively assigned to be derived from brachiopods. Despite showing good structural preservation, the Konrad #101 core shell material does not fulfill the necessary geochemical criteria to be considered as well preserved. None of the fragments shows Mn concentrations < 100 ppm together with Sr concentrations > 600 ppm (Fig. 8). Fe concentrations are exceptionally high and reach values > 1000 ppm. However, the increased Fe may reflect a signature of the depositional environment given that the succession is rich in Fe-bearing ooids reaching exploitable concentrations in certain layers (Berg et al. 1987). In the Konrad #101 core, the shell containing host rock shows higher clay content compared to Bisperode, typically resulting in better shell calcite preservation. On the other hand, the small size of the analyzed shell fragments may have promoted diagenetic overprint.

In summary, combining morphological preservation, CL characteristics, and trace element threshold values, 7 samples from Bisperode (2 brachiopods, 2 trichites, 3 oysters,) were classified as well-preserved and analyzed for strontium-isotope ratios. Although all shell fragments from the Konrad #101

core show signs of diagenetic alteration, we still selected 4 shell fragments with Sr concentrations > 600 ppm for strontium-isotope analysis (Table 1).
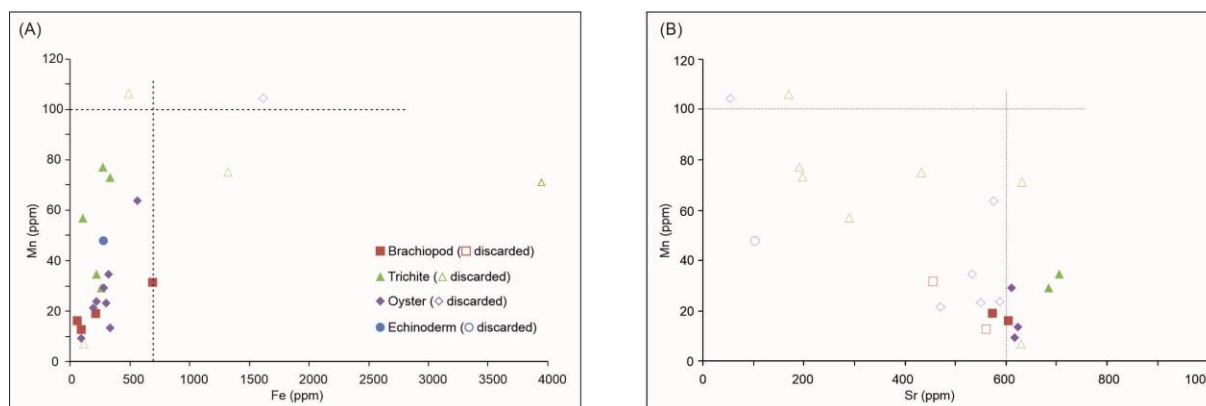

Fig. 7. Trace element composition of different shell materials derived from Bisperode displayed in scatter plots. (A) Mn vs. Fe concentration (in ppm) and (B) Mn vs. Sr concentration (in ppm) for shell material incl. brachiopods, oysters, trichites and echinoderms. Dashed lines in (A) indicate thresholds for Mn at 100 ppm and for Fe at 700 ppm. The dashed line in (B) indicates the threshold for Sr at 600 ppm. Filled symbols refer to samples fulfilling the threshold criteria, and hollow symbols represent samples, which are discarded for further analysis based on trace element composition.

Fig. 8. Trace element composition of different shell fragments derived from Konrad #101 core displayed in scatter plots. (A) Mn vs. Fe concentration (in ppm) and (B) Mn vs. Sr concentration (in ppm) for shell fragments of the unknown taxonomic assignment. Dashed lines in (A) indicate thresholds for Mn at 100 ppm and for Fe at 700 ppm. The dashed line in (B) indicates the threshold for Sr at 600 ppm. Filled symbols refer to samples fulfilling the threshold criteria, and hollow symbols represent samples, which are discarded for fur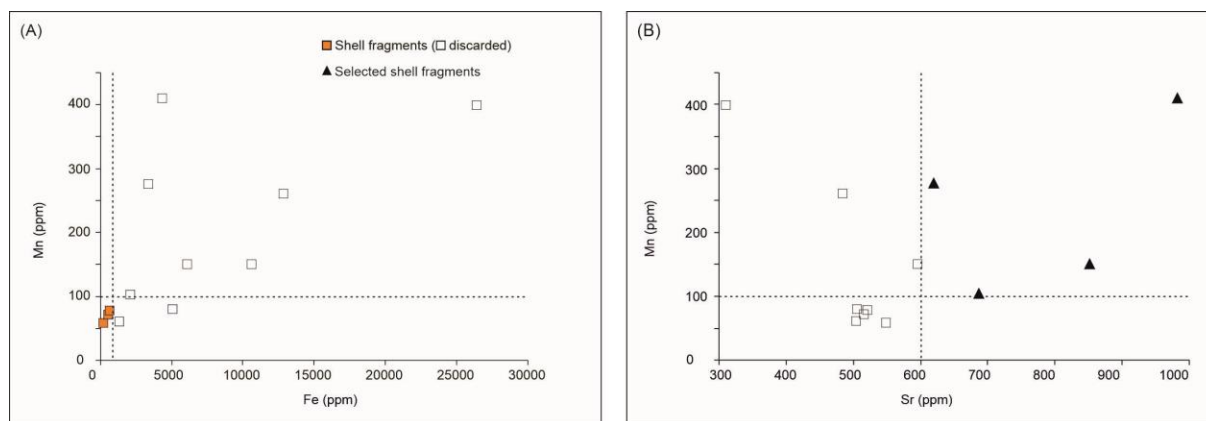ther analysis based on trace element composition. Filled triangle symbols selected sample for strontium-isotope analysis.

4.6.2 Numerical age constraints

Bruhn et al. (2005) presented $^{87}Sr/^{86}Sr$ ratios of echinoid fragments and interparticle cement from the Korallenoolith Fm. with $^{87}Sr/^{86}Sr$ ratios varying from 0.706910 to 0.708064, which have been interpreted to represent the original marine water composition. Rais (2007) performed $^{87}Sr/^{86}Sr$ ratio analyzes on well-dated belemnites covering Late Callovian to Oxfordian strata derived from Switzerland, France, and northern Italy. In their study, $^{87}Sr/^{86}Sr$ ratios range between 0.706897 and 0.706821. The observed Sr-isotope trend in our study is in good agreement with the lower ratios of Bruhn et al. (2005) and in the same range as the data of Rais (2007), which corresponds to a Late Jurassic age range. Compared to the Late Jurassic open ocean Sr-isotope curve of McArthur et al. (2020), all the data points from the LSB deviate from the open marine Sr-isotope record and fail to provide a definitive age assignment (Fig. 9; Fig. 10). Hence, the Sr-isotope data obtained from Bisperode and the Konrad #101 core cannot be used to confirm or refine the existing biostratigraphic age assignment of the Korallenoolith Fm.
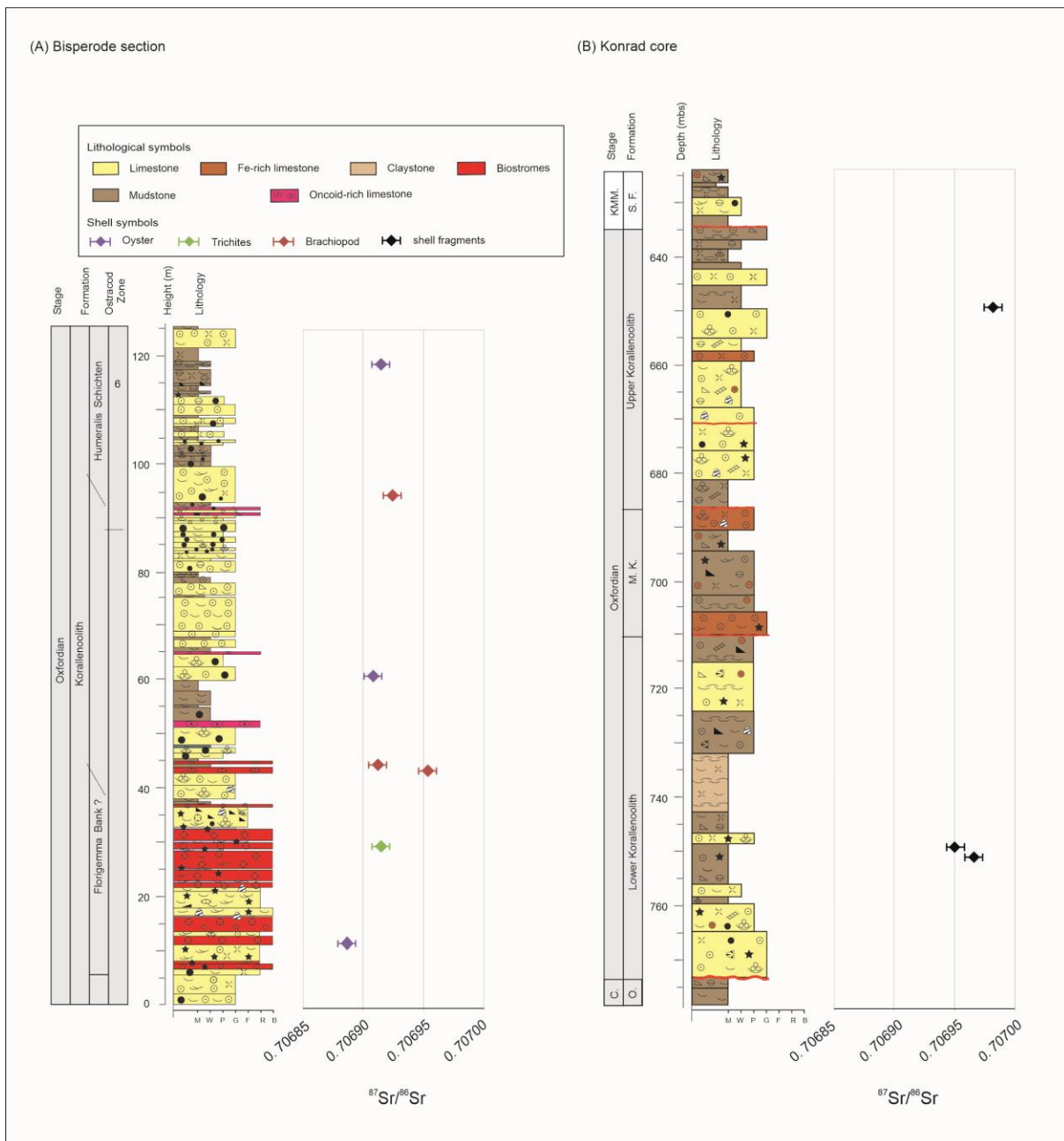
Fig. 9. Lithostratigraphy versus $^{87}Sr/^{86}Sr$ ratios of selected calcite shell materials for (A)Bisperode section and (B) Konrad #101 core. For details of sedimentary log symbols, see Chapter 2 and Chapter 3.
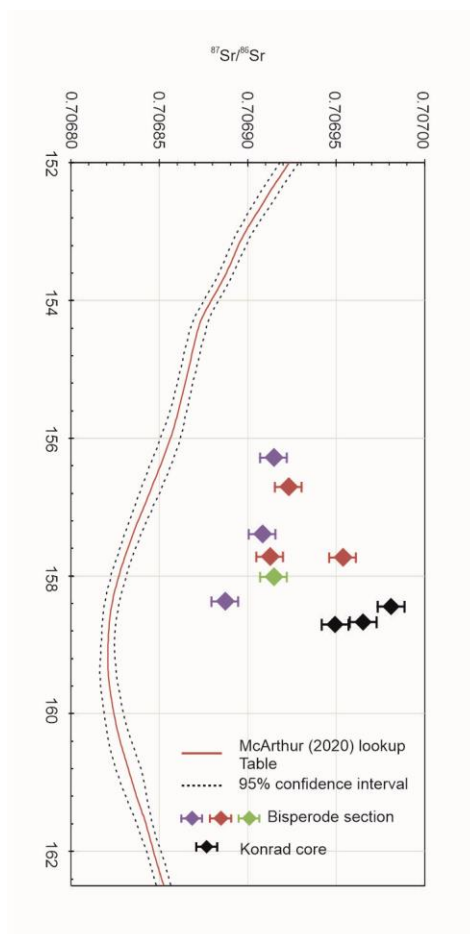

Fig. 10. Analyzed $^{87}Sr/^{86}Sr$ ratios obtained from the Oxfordian Korallenoolith Fm. (Bisperode section and Konrad #101 core, LSB) compared to the LOWESS best-fit curve of McArthur et al. (2020). Y-axis shows age in millions of years.

4.6.3 Regional factors affecting mollusc shell $^{87}Sr/^{86}Sr$ ratios and their implications

During the Oxfordian stage, the LSB was surrounded by emerged land masses (incl. the Ringkøbing Fyn High to the north and the London-Brabant, Rhenish, and Bohemian massifs to the south). The marine waters of the LSB could have been easily affected by the input of freshwaters carrying a continental radiogenic Sr-isotope signature to the basin. The deposition of the Korallenoolith Fm. occurred coeval to changes in climatic conditions, forcing the erosion of the hinterland and leading to increased nutrient input into the depositional setting (Gramann et al. 1997; Kästner et al. 2010). This could have significantly influenced the $^{87}Sr/^{86}Sr$ composition of local marine waters, in particular in areas close to freshwater discharge. Consequently, inputs of more radiogenic Sr from rivers (continental flux with high radiogenic $^{87}Sr/^{86}Sr$ ratios) may have resulted in slightly more radiogenic Sr-isotope ratios in the analyzed shell materials. In the LSB, all the measured $^{87}Sr/^{86}Sr$ ratios are highly radiogenic compared to Oxfordian global open ocean $^{87}Sr/^{86}Sr$ isotopic signatures (McArthur et al. 2020). Hence, the observed pattern from the LSB is best assigned to freshwater mixing. Alteration due to diagenetic

fluids is an alternative explanation for the slightly more radiogenic values observed in the shell calcite. The LSB underwent tectonic inversion (Ziegler, 1987, 1995; Sippel et al., 2009; Kneuker et al. 2020), which was accompanied by to strong uplift, the development of fracture systems and salt diapirism, which all together could have enhanced fluid flow and sediment alteration. However, the strong diagenetic overprint of the studied shell material is not supported by the good structural preservation of shell calcite and by the trace element result.

4.7 Conclusions

In this paper, we present a new calcite shell-based $^{87}Sr/^{86}Sr$ data-set based on well-preserved skeletal materials. The new $^{87}Sr/^{86}Sr$ values stem from low-Mg calcite brachiopods, oysters, and *trichites* bivalves and are within the range of values reported for Late Jurassic seawater. However, closer inspection shows a distinct deviation from the Oxfordian marine Sr-isotope signal, indicating that the depositional setting was probably influenced by freshwaters with a continental Sr-isotope signature. The analysed shells may have captured local, more radiogenic $^{87}Sr/^{86}Sr$ signatures derived from riverine waters. Our $^{87}Sr/^{86}Sr$ results indicate that shells from shallow marine settings showing no diagenetic overprint can still show deviation from the normal marine Sr isotope signature.

4.8 Acknowledgments

4.9 References

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5. Carbon isotope stratigraphy of an Oxfordian carbonate ramp system, Lower Saxony Basin, Northern Germany

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5.1 Abstract

Shallow carbonate deposits represent highly sensitive ecological systems and can provide valuable information for understanding the climate system and sea-level changes in the geological past. However, decoding these archives can be challenging due to the low stratigraphic resolution achieved through biostratigraphy. This is particularly the case for the Late Jurassic carbonate deposits of the Lower Saxony Basin, where the lack of typical index fossils hinders precise correlations between different sections. Carbon isotope ($\delta^{13}C$) stratigraphy has been applied as a reliable tool for comparing and calibrating biostratigraphic schemes on both, local and global scales. In this study, high-resolution $\delta^{13}C$ analyses of bulk carbonate from three outcrop sections are investigated and a $\delta^{13}C$ chemostratigraphy correlation panel is presented for the Oxfordian Korallenoolith Formation. The chemostratigraphic data presented here enable the confirmation and refinement of the pre-existing biostratigraphic data and the establishment of a composite high-resolution stratigraphic framework enhancing the correlation ability between the western and eastern part of the LSB. Overall, this framework allows also to better comprehend what might have been the impact of the carbon cycle disturbances on the Late Jurassic shallow-marine carbonate systems.

Keywords: Shallow-water carbonates, Carbon isotope stratigraphy, Oxfordian, Lower Saxony Basin

5.2 Introduction

During the Oxfordian stage (154.8-161.5 Ma, Gradstein et al. 2020), the Lower Saxony Basin (LSB) was covered by a shallow epicontinental sea under a subtropical climate (Ziegler, 1990). The shallow-marine deposits are sedimentary successions composed of alternating limestones, marls, and recifal carbonates and correspond to the Korallenoolith Formation (Fm.). Despite multiple biostratigraphic schemes that have been developed over the years, the detailed stratigraphy and subdivision of the Upper Jurassic rocks of the LBS are still poorly defined (Schudack, 1994; Weiß, 1995; Gramann et al., 1997; Mudroch et al., 1999; Luppold, 2003). The shallow-marine strata lack typical open-marine index fossils and the prevalence of sedimentary gaps in the Korallenoolith Fm. further hampers any lithostratigraphic subdivision of the Korallenoolith sequence (Gramann et al. 1997). As ammonites are very scarce or lacking, other biostratigraphic schemes have been developed, including schemes based on ostracods, benthic foraminifera, charophytes, terrestrial and marine palynomorphs, and vertebrate remains (e.g., Schudack, 1994; Weiß, 1995; Gramann et al., 1997; Mudroch et al., 1999; Luppold, 2003). However, most of those organism groups are endemic, and due to the facies-controlled restriction, any correlation on a supra-regional and/or global scale remains ambiguous and imprecise (Jach et al., 2014). As a result, a precise stratigraphic age assignment of the Korallenoolith Fm. in the LSB is still difficult, although some excellent Upper Jurassic sections are exposed in the LSB, including the Bisperode section (Ith syncline), the Osterwald section and the outcrops of the Langenberg quarry.

Carbon isotope ($\delta^{13}C$) records obtained from Mesozoic shallow-water carbonates have been widely used as a proxy for secular changes in ocean chemistry. Unfortunately, carbonate $\delta^{13}C$ signatures derived from shallow-water settings are often afflicted with large uncertainties, compared with hemipelagic and pelagic succession (Huck et al., 2011; Horikx et al., 2014; Frijia et al., 2015; Huck and Heimhofer, 2015; Bover-Arnal et al., 2016; Zuo et al. 2018). Post-depositional diagenetic alteration and/or environmental controls on the $\delta^{13}C$ signature need to be treated carefully. In addition, shallow-water carbonates may record local seawater carbon isotope signatures (Patterson and Walter, 1994; Immenhauser et al., 2003), and the signals extracted from shallow-water carbonates, especially those from lagoonal and peritidal settings, make the application of carbon isotope stratigraphy even more challenging (Coimbra et al., 2016). Despite these obstacles, many studies using $\delta^{13}C$ values from shallow marine carbonates demonstrate the preservation of a global marine carbon isotope signature and support a correlation between shallow-water and deep-water successions for stratigraphic purposes (Vahrenkamp, 1996; Weissert et al. 1998; Glumac and Walker, 1998; Grötsch et al.1998; Huck et al. 2011; Buonocunto et al. 2002; Immenhauser et al. 2002; Krullet al. 2004; Swart and Eberli, 2005; Huck and Heimhofer 2015; Coimbra et al., 2016; Huck et al. 2017; Zuo et al. 2018). Most studies focus on characteristic isotope signatures and stratigraphic trends rather than on absolute values (Immenhauser et al. 2003; Huck et al. 2011).

Chemostratigraphic studies dealing with Oxfordian strata are comparatively rare, and only a limited amount of carbon isotope data is currently available (Wierzbowski et al., 2017). During this time period, the western European archipelago and its adjacent shallow seas experienced significant ecological changes, expressed in the onset of widespread carbonate sedimentation and the global spread of coral

reefs (Leinfelder 2001; Helm et al. 2001; Betzler et al. 2007; Martin-Garin et al. 2012). However, precise dating and correlation of such changes in carbonate platform ecology at different sites (e. g. Jura Mountains, North German basin, Paris basin, England Yorkshire and Cambridgeshire) are problematic due to insufficient temporal resolution (Helm et al. 2003a).

In the LSB, regional synsedimentary salt tectonism and induced fluctuations in sedimentation rates complicate stratigraphic comparison and correlation with the Boreal Ocean during the Oxfordian (Hoyer, 1965; Betz et al. 1987; Gramann et al., 1997). The combination of chemostratigraphic (carbon isotopes) data with biostratigraphic information represents a promising approach to better date and correlate strata across different local depositional environments (Huck et al. 2011; Horikx et al. 2014; Frijia et al. 2015; Schmitt et al. 2020).

Up to now, some high-resolution carbon isotope stratigraphic records have been established for the Upper Jurassic strata of the LSB (Kästner et al., 2010; Bai et al. 2017; Zuo et al. 2018), but only Zuo et al. (2018) used chemostratigraphy to establish a refined stratigraphic framework for the investigated successions. Carbon isotope records covering the Oxfordian deposits within the LSB are scarce, with only three publications reporting continuous carbon isotope curves from outcrop or core material (Kästner et al., 2010; Bai et al. 2017, 2020), and a convincing carbon isotope-based intrabasinal correlation of the Korallenoolith Fm. across the LSB is still lacking. In this study, new data from the lower part of the Bisperode section, the lower Langenberg section, the Osterwald section, and the Konrad #101 core will be compared with existing data sets from the Eulenflucht 1 (Heunisch and Luppold, 2015; Bai et al., 2017). The overall objective of this study is the development of a high-resolution carbon isotope stratigraphic record for Oxfordian successions in the LSB. The new and refined correlation will shed light on the stratigraphic development of the Korallenoolith depositional system within the LSB and beyond.

5.3 Geological setting

The LSB located on the southern margin of the Central European Basin is one of several rift- and wrench-induced ''marginal troughs'', that formed a series of E-W trending horst-and-graben structures (Voigt 1962; Betz et al., 1987; Ziegler 1990; Senglaub et al., 2006). The LBS has a length of ~300 km and a width of ~65 km and was bordered by the Rhenish Massif to the S and the Ringkøbing-Fyn High to the N (Zuo et al. 2018) (Fig. 1a). Sediment thickness reaches a maximum of ~4000 m (Betz et al. 1987; Kästner et al., 2010). Stratigraphic sections located on the uplifted horst regions may contain fewer small- and medium-scale cycles compared to the adjacent graben areas (Kästner et al. 2008). During the Oxfordian, the LSB was located at a palaeolatitude of about ~ 35°N (van Hinsbergen et al. 2015) and formed a tributary sea of the Tethys, which allowed the interchange of fauna and flora between the Boreal and the Tethyan realms (Helm et al. 2001; Cäsar, 2012). Upper Jurassic deposits are mainly exposed in the E' part of the LSB with good and well accessible outcrops in the low mountain ranges of S' Lower Saxony. The studied stratigraphic sections include the Langenberg section, which is located in an active quarry about 5 km E of Goslar, the Bisperode section accessible in an abandoned quarry located about 2 km SW of the village Lauenstein, and the Osterwald section located in an abandoned quarry about 3 km SW of the village Springe Holtensen. The new results are compared with

carbon isotope data from the scientific drill core Konrad #101, which was drilled close to the village Salzgitter-Beddingen (Fig. 1).
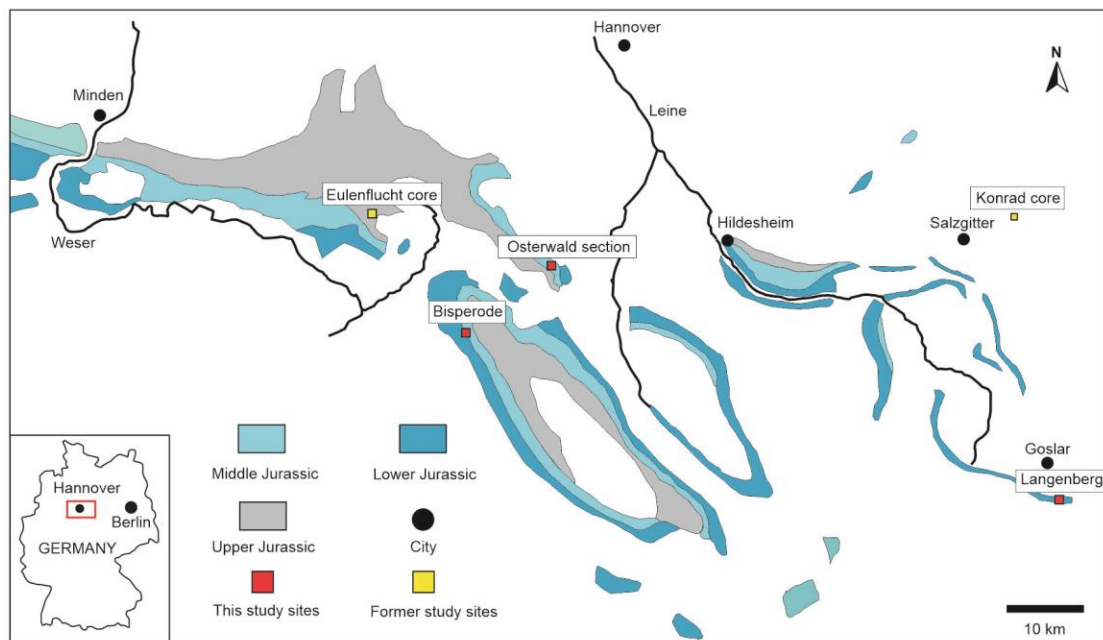

Fig. 1. Simplified geological map of Lower to Upper Jurassic strata cropping out in the central part of the southern Lower Saxony Basin. Locations of the investigated study sites and sites used for comparison are marked by red and yellow dots, respectively.

In the LSB, the Upper Jurassic succession includes the lithological units of the Upper Ornatenton Fm. (Callovian), Heersumer and Korallenoolith Fm. (Oxfordian), the Süntel Fm. (Kimmeridgian), Holzen Fm. and Eimbeckhausen Fm. (Tithonian). Focus of this study is on the limestones of the Oxfordian Korallenoolith Fm. (Middle to Late Oxfordian) (Fig. 2). The Korallenoolith Fm. consists predominantly of oolithic limestones with coral reef-bearing intercalations, assigned to a shallow-marine subtropical environment with limited terrestrial influx, which was deposited on a homoclinal carbonate ramp system (Helm et al. 2003; Betzler et al. 2007; Kästner et al. 2008; Cäsar et al. 2012; Zuo et al. 2018).

The biostratigraphic subdivision of the Upper Jurassic strata in Northern Germany was developed based on ammonites, ostracods, dinoflagellate cysts, charophytes, spores, and pollen (Schudack 1994; Weiß 1995; Gramann et al. 1997; Hardenbol et al. 1998). Due to the rare occurrence of age-diagnostic ammonites, the Oxfordian strata in the LSB is divided based on ostracods with the ostracod zones 1 to 8 covering the Ornatenton Fm. (zone 1), the Heersumer Fm. (zones 2 and 3), and the Korallenoolith Fm. (zones 4 to 8). The correlation between the ostracod zones from Gramann et al. (1997) and the sub-boreal ammonite zones as well as the diachronous character of the lower and upper boundaries of the Korallenoolith Fm. are shown in Fig. 2.

Fig. 2. Lithostratigraphic scheme of the Late Jurassic and its correlation with the standard zonation of the sub-boreal ammonite provinces (modified from Gramann et al. 1997; Hardenbol et al. 1998; Schulze 1975; Gradstein and Ogg 2020) and Ostracod zonation (Schudack 1994; Weiß 1995).

5.4 Lithostratigraphy and carbonate facies description

5.4.1 Bisperode section

For the Bisperode section, we focus on the lower 126 m of the accessible section (Fig. 3), assigned to the Korallenoolith Fm. (Betzler et al. 2007; Cäsar 2012), detailed sedimentology and sequence-stratigraphy are presented in Chapter 2. The lowermost interval (0.0–5.5 m) are represented by thick-bedded oolitic grainstones with large-scale cross-bedding and abundant shell detritus. Above, (5.5-45.0 m) characterized by boundstone horizons alternate with bioclastic-rich rudstone. The boundstone layers show distinct variations in terms of growth form (ramose, flat sheet-like, dome-shaped, hemispheric) and texture of the dominant reef builders. and bioclastic-rich rudstone beds (>1 m thickness) typically show fining-upward units and trough cross-bedding. In the third interval (45.0–65.0 m), grain- and packstone textures dominate the succession, with some intervals showing a high portion (>50%) of large benthic agglutinated *Reophacidae cf. Reophax* foraminifera. The marl-limestone alternation intervals at 52.6–60.0 m, 99.5 m–103.5, and 112.5 m–121.5 m are characterized by wacke- to mudstone beds. The upper part of the section (66.0 to 125.5 m) is essentially composed of ooid-rich pack- and grainstones with intercalations of bioclastic-rich wackestone.
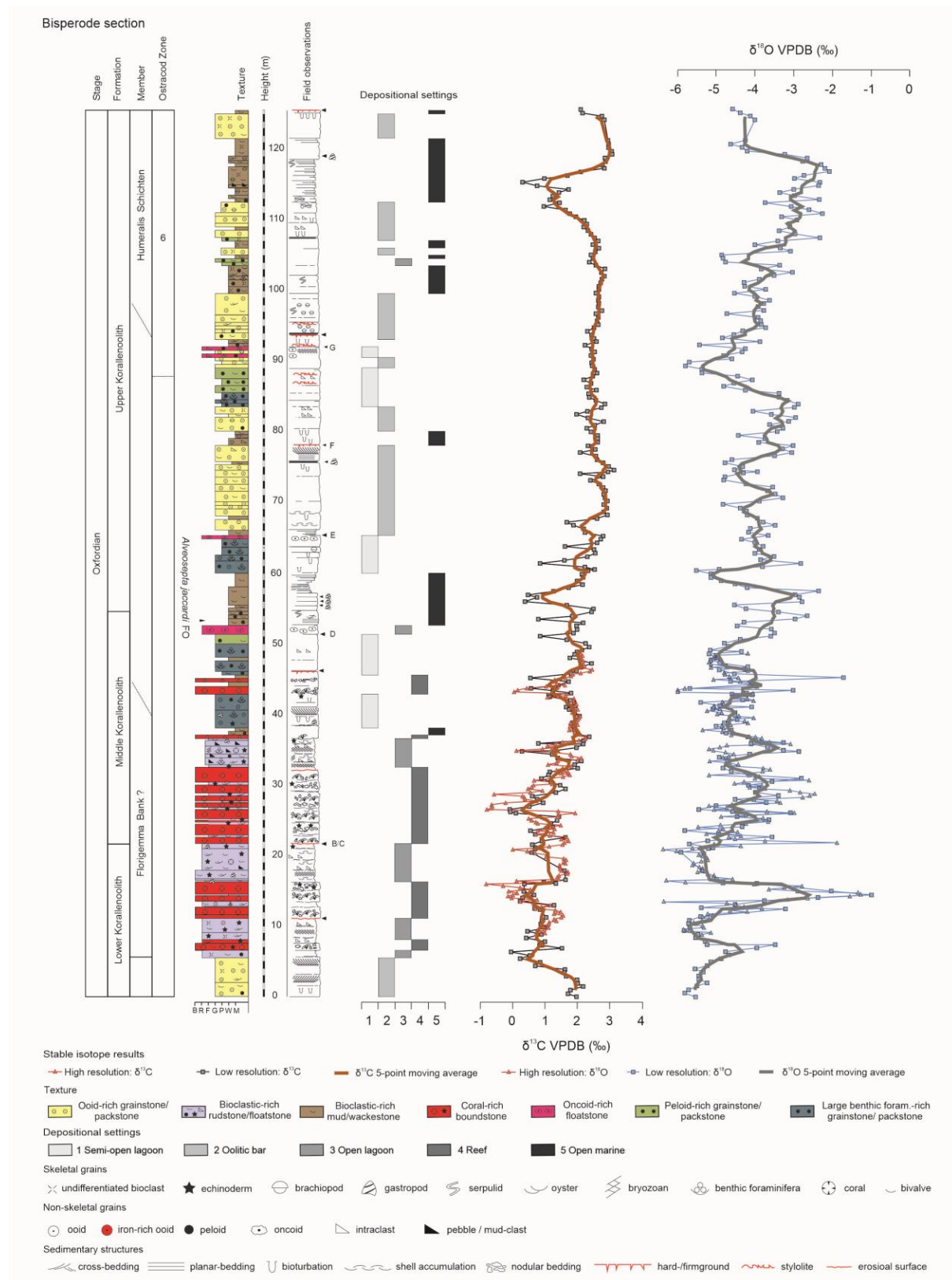
Fig. 3. Lithostratigraphy, sedimentological observations, erosional profile, inferred depositional settings, δ13C and δ18O values of the Bisperode section illustrated against stratigraphic height (m).

5.4.2 Osterwald section

Based on characteristic microfacies associations, biota content, and the position of discontinuity surfaces, the 46 m thick Osterwald section can be divided into 3 stratigraphic members (Mbs.) (Helm et al. 2003) (Fig. 4). The lower part is assigned to the Ahrensberg-Mb. (0.0–26.0 m), which is composed of two types of lithologies. The basal, 4 m thick part is composed of alternating thick grainstone beds alternating with thin marly layers, containing abundant fossil fragments incl. echinoderms, oysters, serpulids, plant remains, and rarely belemnites. This interval characterizes the very base of the Korallenoolith Fm. and its transition towards the underlying Heersum Fm. (Kaiser 1979; Schormann and Zawischa 1990). The upper 22 m thick part is composed of high-energy shoal limestones, which are represented by thick-bedded grainstones with large-scale cross-bedding and abundant shell detritus (echinoderm and mollusk fragments). This interval is bound by a hardground with strong bioturbation and high fossil density. The middle Hainholz Mb. (26.0–38.0 m) includes coral boundstones, intercalated with reef flank bioclastic rud- to floatstones. The boundstone intervals are dominated by flat, sheet-like, and strongly recrystallized corals, often showing abundant bioerosion features (for more details see Helm et al. 2003). The uppermost Barenburg-Member (38.0–46.0 m) is made up of ooid-rich packstones. In this study, the focus is on Ahrensberg and Hainholz Mbs. A detailed sedimentological study incl. a sequence-stratigraphic interpretation of the Osterwald section is provided by Helm et al. (2003).
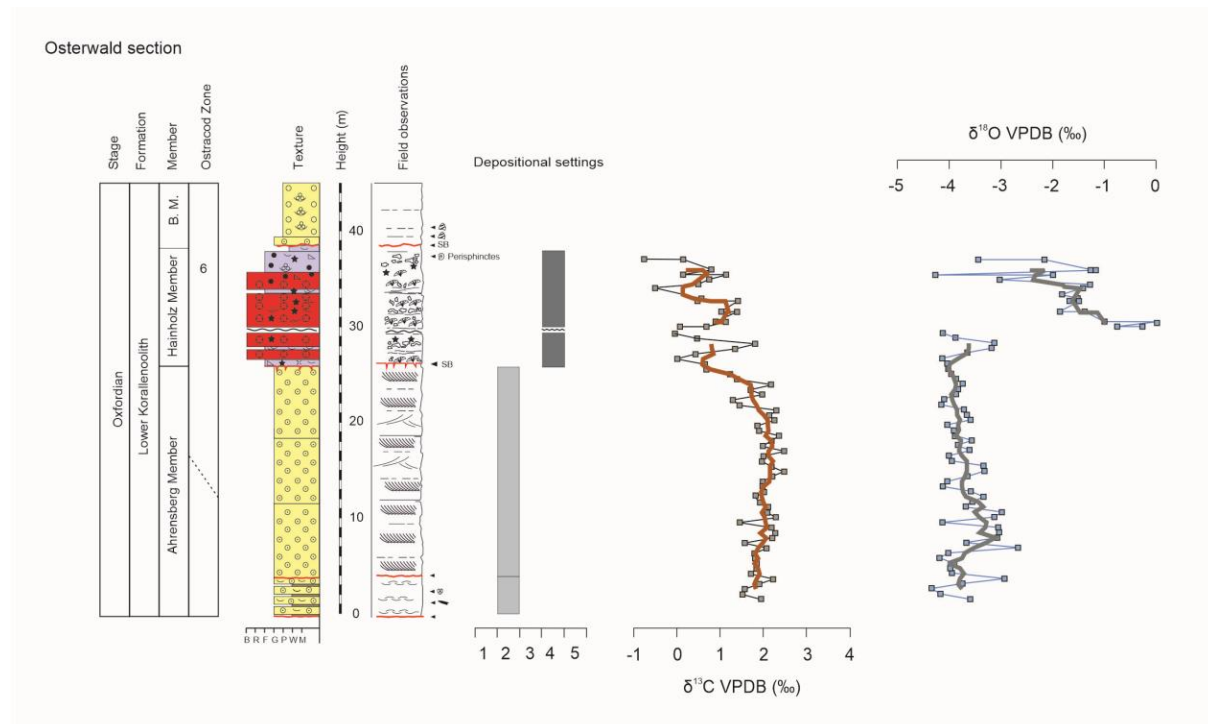

Fig. 4. Lithostratigraphy, sedimentological observations, erosional profile, inferred depositional settings, $\delta^{13}C$ and $\delta^{18}O$ values of the Osterwald section illustrated against stratigraphic height (m).

5.4.3 Langenberg section

In the studied part of the Langenberg section, 3 different lithostratigraphic units were identified within the 16 m thick section of the Korallenoolith Fm. (Fig. 4). The lowermost interval (0.0–2.0 m) is characterized by a thin-bedded, dark-grey clay to marlstone with rare shell fragments. This unit is bound by an erosional surface and overlain sharply by the second unit (2.0–10.0 m). This unit is mainly composed of well-developed oncoides, with individual beds showing large-scale cross-bedding and abundant shell fragments (bivalve and serpulid fragments), rare quartz, and Fe-rich peloids. Above, unit 3 (10.0–14.0 m) is characterized by thick-bedded oolitic grainstones. Common sedimentary features include cross-bedding, channel structures, and burrows. The fossil content in unit 3 comprises allochthonous macrofauna (echinoderms, bivalve shells) as well as abundant unidentified shell fragments. Unit 4 (14.0–16.0 m) is again composed of well-developed oncoides, similar to unit 2. The uppermost unit 5 (16.0–19.0 m) is made up of thick-bedded oolitic grainstones, which resemble unit 4.
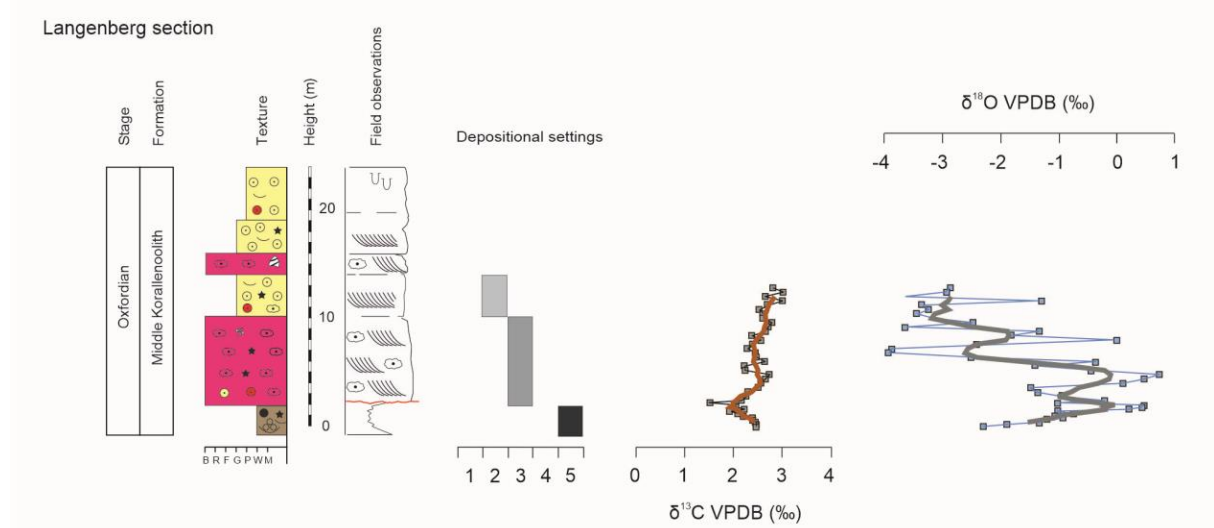
Fig. 5. Lithostratigraphy, sedimentological observations, erosional profile, inferred depositional settings, $\delta^{13}C$ and $\delta^{18}O$ values of the Langenberg section illustrated against stratigraphic height (m).

5.5 Materials and methods

5.5.1 Fieldwork and sampling

Fieldwork was carried out in three well-accessible quarries. Individual sections were logged in stratigraphic order and on the scale of individual beds incl. detailed macroscopic descriptions. Bulk samples taken with the hammer and drilled powder samples were taken with a battery-driven driller. Samples were taken bed by bed with a sampling interval of ~0.5 m or less. Higher density sampling was performed across facies boundaries and discontinuities. A total of 257 bulk samples were collected across the ~126.0 m thick Bisperode section. In addition, 164 drilled powder samples were obtained from the lower part of of the section (at a spacing of ~0.25 m) for comparison. In the ~46 m thick Osterwald section, 14 bulk rock samples and 53 drilled powder samples were collected. The ~16 m thick

Langenberg section was covered with 39 drilled powder samples. For limestone classification, the scheme of Dunham (1962), including the modifications by Embry and Klovan (1971), was used. Bulk samples were washed and air-dried on the sample shelves, and subsequently cut into slabs for petrographic thin-sections.

Bulk rock sample powders were obtained (i) directly in the field using a hand-held battery-driven driller (163 samples from Bisperode, 53 from Osterwald, 39 from Langenberg), (ii) in the laboratory using a vibrating ball mill (258 samples from Bisperode), (iii) in the laboratory using a micro-driller equipped with tungsten drill bits (37 from Osterwald).

5.5.2 Isotope analysis

Carbon and oxygen isotopic analyses were carried out on a total of 577 powder samples at the stable isotope laboratory of the Institute of Geology at Leibniz University Hannover, Germany. All sample powders were treated with 100% phosphoric acid at 72 °C for at least 45 min. Stable isotope analysis were conducted using a Thermo Fisher Scientific Gasbench II carbonate device connected to a Thermo Fisher Scientific Delta 5 Advantage isotope ratio mass spectrometer. Repeated analyses of certified carbonate standards (NBS 19, IAEACO-1, NBS 18, and Carrara Marble) show an external reproducibility of $\leq$0.06 ‰ for $\delta^{13}C$ and 0.08 ‰ for $\delta^{18}O$. Values are expressed in conventional delta notation relative to the Vienna-Pee Dee Formation belemnite (VPDB) international standard, in parts per mil (‰). For more details on the analytical procedure, we refer to Schmitt et al. (2020). For the purpose of chemostratigraphic correlation, a 5-point moving average stratigraphic trend was calculated from all measured carbon and oxygen isotope values ($\delta^{18}O$).

5.6 Stable isotope results

5.6.1 Bisperode section

The $\delta^{13}C$ record of the Bisperode section varies between -0.1 ‰ and 3.1 ‰ (mean: 1.6 ‰) and shows distinct variations across the studied section (Fig. 3). In general, carbon isotope fluctuations are stronger in the lower and middle Korallenoolith Fm. compared to the upper Korallenoolith Fm. The lower part (0.0–68.0 m) is characterized by alternating negative and positive shifts with $\delta^{13}C$ values ranging between -0.1 ‰ and 3.0‰, with a superimposed stepwise increase. In the upper part (68.0–109.0 m), the carbon isotope record shows a pronounced plateau with relatively stable values of ~2.5 ‰, and only the top part of the section (109.0–125.0 m) is characterized by a well-developed negative anomaly with an amplitude in the range of 1.5 ‰.

In more detail, the $\delta^{13}C$ trend in the lowermost interval (0.0–5.5 m) is characterized by a distinct negative $\delta^{13}C$ shift of ~2.2 ‰, which is followed by some robust oscillations (5.5–27 m) between -0.1 and 2 ‰. The overlying interval (27.0–38.5 m) exhibits a noticeable stepwise increase with values reaching up to 2.4 ‰. This is followed by a relatively stable trend (38.5–56.5 m), which is interrupted by several smaller-scale negative excursions. The above interval (56.5–70.0 m) is

marked by a sharp negative shift (with an amplitude of 1.6 ‰) and then exhibits a stepwise increase to maximum values of up to 3.1 ‰. The following interval (70.0–99.0 m) is characterized by a distinct δ13C plateau with values oscillating around 2.6 ‰. The uppermost segment (99.0–126.0 m) shows a gradual δ13C decline, reaching a minimum as low as -0.1 ‰, followed by a sharp δ13C increase (up to 3 ‰) .

The δ18O values from the Bisperode section vary significantly between -6.4 ‰ and -1 ‰ (mean: -4.3 ‰) (Fig.3). The δ18O record is characterized by high-amplitude fluctuations of up to 1.5 ‰ within 60 m of section (0.0–60.0 m)). Overall, a trend towards less negative values is observed upsection.

5.6.2 Osterwald section

The δ13C values of samples derived from the Osterwald section range between -0.8 ‰ and 2.5 ‰ (mean: 1.7 ‰) (Fig. 4). The lower part of the section (0.0–26.0 m) shows relatively stable δ13C values, of ~2 ‰ with only minor oscillations. The subsequent segment (26.0–33.0 m) is characterized by a noticeable stepwise negative shift reaching values of ~0.5 ‰. The uppermost part (33.0–37.0 m) shows strong fluctuations around values of ~0.8 ‰.

The δ18O values from the Osterwald section vary between 0 ‰ and -4.4 ‰ (mean: -3.7 ‰) (Fig. 4). The lower part (0.0-33.0 m) displays relatively negative values with a trend toward more negative values upsection. This contrasts with the upper segment (33.0–37 m), which shows the highest δ18O values (0 ‰) at its base, followed by a gradual shift towards more negative values as low as -4.3 ‰.

5.6.3 Langenberg section

The δ13C values of the Langenberg section show only minor variability and range between 1.4 % and 3.0 % (mean: 2.4 %) (Fig. 5). The lowermost part (0.0–2.0 m) is characterized by an apparent gradual decline, reaching 1.4 ‰. The overlying segment (2.0–13.0 m) shows a stepwise increase toward more positive δ13C values reaching 3 %.

δ18O values from the Langenberg section vary between -4 ‰ and +0.7 ‰ (mean: -1.6 ‰) and are characterised by strong fluctuations. Records a positive extrusion (0.0–6.0 m) and then a stepwise negative shift (6.0–13 m) (Fig. 5).

5.7 Discussion

5.7.1 Reliability of the carbonate carbon and oxygen isotope data

In general, δ18O values of shallow marine carbonates have to be treated with caution due to potential diagenetic modification (compared to carbon) given the rapid exchange with the oxygen from the surrounding pore fluids (Allan and Matthews, 1982; Banner and Hanson, 1990; Jenkyns et al. 1994; Immenhauser et al., 2002; Weissert et al., 2008; Huck et al. 2013). Meteoric as well as burial diagenesis can lead to concomitant decrease in the 18O content of carbonate rocks (Colombié et al., 2011). This may explain why the analyzed δ18O values depart from typical Late Jurassic marine δ18O

signatures derived from well-preserved Oxfordian belemnites (Padden 2001; Nunn and Price 2010; Price and Rogov 2009; Benito et al. 2012), diagenetically unaltered ammonites (Wierzbowski et al., 2013), and oysters (Brigaud et al., 2008). The observed trend towards more depleted $\delta^{18}O$ values observed in the Osterwald and Bisperode sections indicates a certain diagenetic overprint (Fig. 6). Hence, due to a clear diagenetic influence on the $\delta^{18}O$ signatures, this type of data will not be further discussed in this study.

The analyzed bulk carbonate samples derived from the Bisperode section show $\delta^{13}C$ values between -0.8 ‰ and 3.1 ‰, between -0.8 ‰ and 2.5 ‰ for the Osterwald section and between 1.4 ‰ and 3.0 ‰ for the Langenberg section (Fig. 6). Such values are considered within the typical range of well-preserved and diagenetically unaltered Oxfordian belemnites (Padden 2001; Nunn and Price 2010; Price and Rogov 2009; Benito et al. 2012), ammonites (Wierzbowski et al., 2013) and oysters (Brigaud et al., 2008). A strong positive correlation between $\delta^{18}O$ and $\delta^{13}C$ values is commonly taken as indication of diagenetic alteration under the influx of meteoric waters within the mixing zone (Allan and Matthews, 1982), or during burial diagenesis (Derry, 2010). The stable isotope records from the studied Korallenoolith sections show only low covariance between $\delta^{13}C$ and $\delta^{18}O$ values (Bisperode section: $r^2=0.0038$; Osterwald section: $r^2=0.1955$; Langenberg section: $r^2=0.1253$), which is interpreted to reflect the absence of strong diagenetic alteration of the stable isotope ratios, potentially exhibiting reliable patterns useful for chemostratigraphic correlation. Relatively low and strongly fluctuating $\delta^{13}C$ values underlying sedimentary discontinuities have often been linked to meteoric diagenesis below subaerial exposure surfaces (Allan and Matthews,1982; Lohmann, 1988). Although in the coral reef-rich lithologies of the Bisperode section (5.5–46.0 m) and upper part of the Osterwald section (26.0–38.0 m), $\delta^{13}C$ shows extensive fluctuations characterized by stronger dolomitization. Also, the inspection of petrographic thin-sections from these intervals indeed reveals the occurrence of vadose diagenetic fabrics typically associated with subaerial exposure episodes. Carbonates underlying subaerial exposure surfaces show negative carbon isotope values, which is likely the result of meteoric diagenesis due to incorporation of light, soil-derived carbon. However, this type of alteration is stratigraphically restricted to a few distinct horizons and did not significantly alter the overall $\delta^{13}C$ trend. Based on the above evidence, the $\delta^{13}C$ signatures of the studied carbonates are considered to represent the $\delta^{13}C$ of the marine dissolved inorganic carbon during the time of carbonate precipitation and therefore can serve as chemostratigraphic signal.
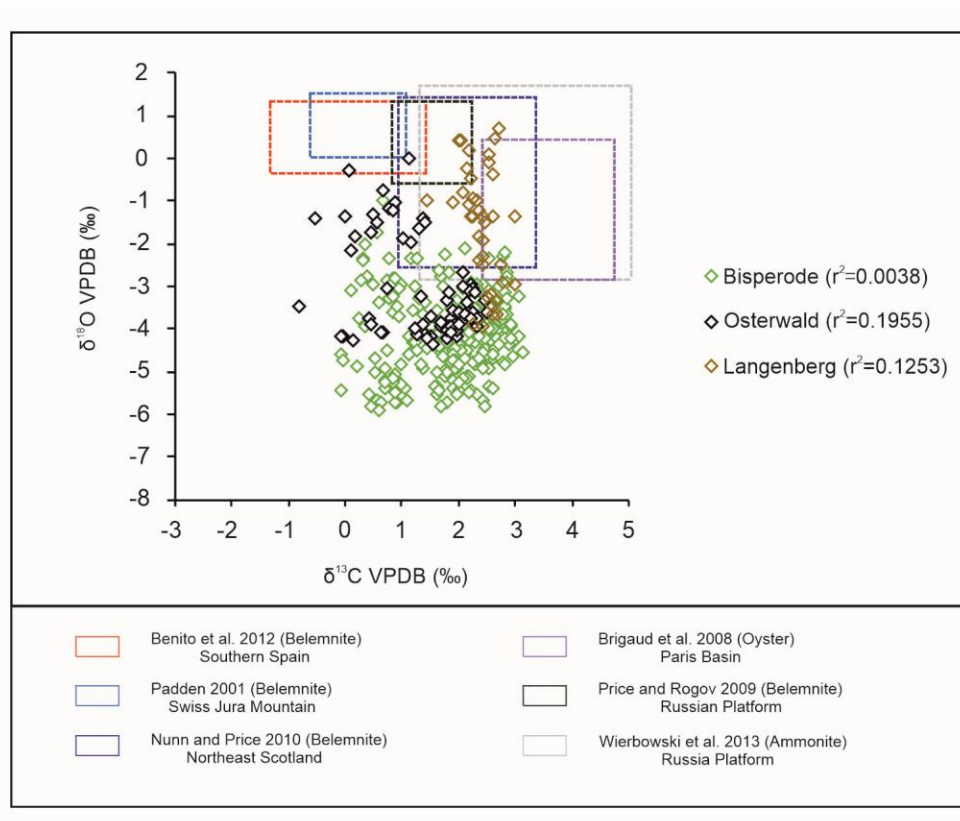
Fig. 6. Cross-plot of δ¹³C and δ¹⁸O values derived from the Bisperode, Langenberg and Osterwald sections compared with data obtained from well-preserved Oxfordian belemnites (Padden 2001; Nunn and Price 2010; Price and Rogov 2009; Benito et al. 2012), ammonites (Wierzbowski et al., 2013) and oysters (Brigaud et al., 2008).

5.7.2 Local environmental effects on carbon isotope signatures

Coastal depositional settings often receive sedimentary contributions from multiple sources and may record the superposition of local and global geochemical signals (Immenhauser et al., 2003; Colombié et al., 2011; Coimbra et al., 2016; Zuo et al. 2018). By comparing the δ¹³C composition in relation to different sedimentary settings, facies-dependent variability of carbon isotope ratios can be identified.

The δ¹³C values obtained from the semi-open lagoon depositional setting show only a slight deviation between the different sections (Fig.7, Bisperode, Langenberg). In such depositional environments with limited connectivity to open marine waters and low freshwater input, along with a high burial rate of organic matter and an oxygen-limited environment, also microscope inspections suggest good preservation of larger benthic foraminifera and other fossils which implies that they are good isotopic markers? The oolitic bar depositional setting shows consistently high δ¹³C values in all three sections. Deposition of ooids occurred in a high-energy shoal environment located between the semi-open and the open lagoon environment. The porous and permeable ooid shoals may potentially generate a localized diagenetic-controlled interval. Due to relatively early stabilization of ooid-forming minerals during diagenesis by marine pore waters with only a minor contribution from organically derived light carbon (Armstrong-Altrin et al. 2009), the δ¹³C signals from those ooid-rich lithologies are expected to

represent the marine DIC isotopic composition (Eltom et al. 2018). The carbon isotope data derived from the open lagoonal setting (restricted to Bisperode) shows a much broader scatter and exhibits more depleted $\delta^{13}C$ values, compared with the semi-open lagoon and ooid bar setting. The coral reef deposits exhibit the most depleted $\delta^{13}C$ values. In these two types of settings (open lagoon, reef), early meteoric diagenesis due to subaerial exposure, local changes in the organic matter source, and dolomitization are probably the most important processes affecting the carbon isotope ratios. Carbon isotope values from open marine strata (Bisperode, Langenberg) show moderate variability and relatively similar values between the two sites. Those off-shore deposits are predominantly composed of fine-grained micrites, which are usually compacted and cemented during a very early stage. Given the relatively low initial porosity of those fine-grained sediments, subsequent cementation, and diagenetic alteration are typically low resulting in only moderate diagenetic overprint (Marshall 1992; Immenhauser et al., 2003; Föllmi et al., 2006; Louis-Schmid et al. 2007; Eltom et al. 2018). In consequence, such kind of deposits is considered to preserve the most primary isotopic signal. Despite a certain degree of local environmental effects on the $\delta^{13}C$ signature, the studied carbonate sections are considered reliable recorders of the DIC of the ambient water masses during carbonate precipitation and allow for robust chemostratigraphic correlation.
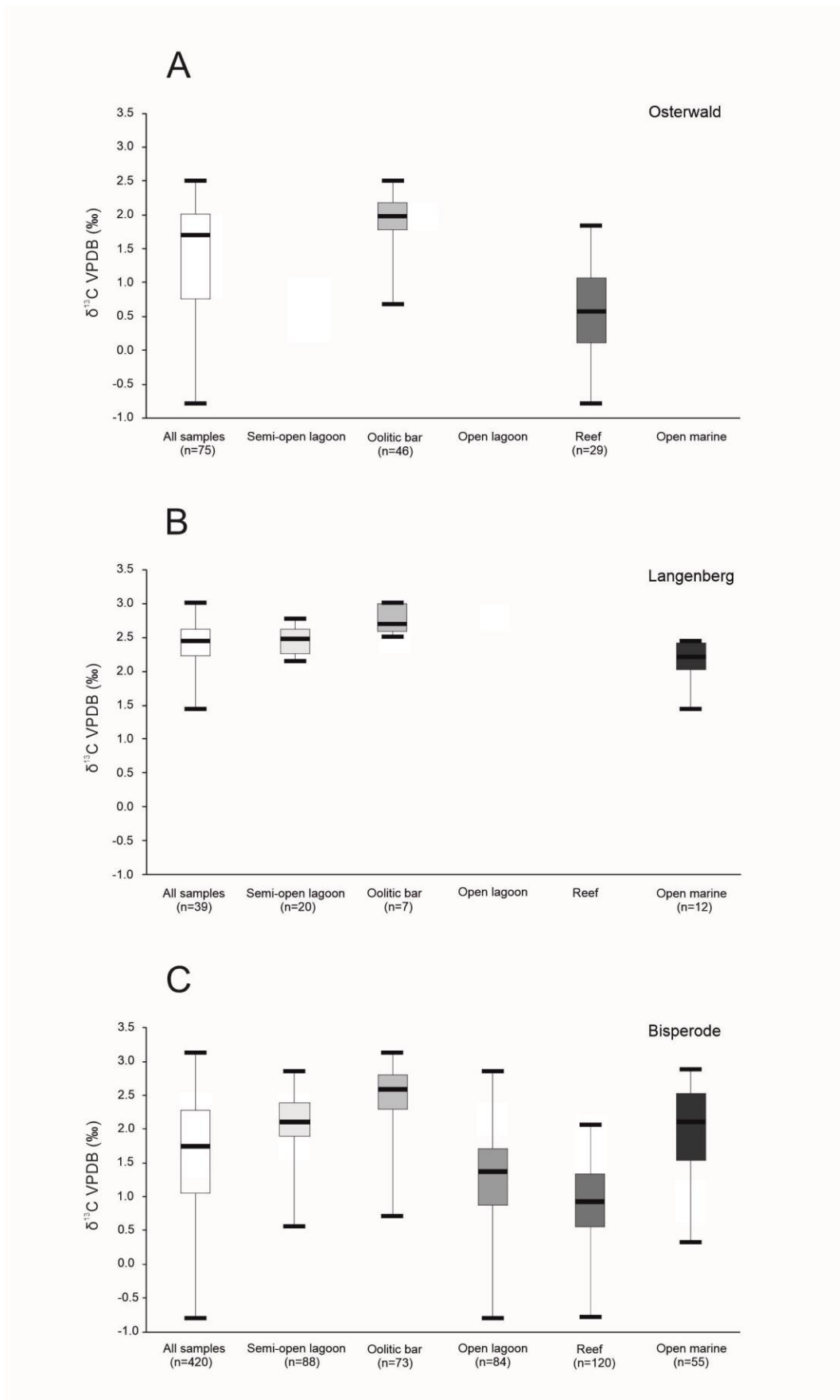
Fig. 7. Variability of δ¹³C values within different carbonate depositional settings for the three studied sections with (A) Osterwald, (B) Langenberg and (C) Bisperode.

5.7.3 Carbon isotope-based correlation within the LBS

The age assignment of the Oxfordian successions within the LSB is primarily based on ostracod biostratigraphy (Heunisch and Luppold 2015; Zuo et al. 2017), with some additional calibration based on $^{87}Sr/^{86}Sr$ ratios for the late Oxfordian to early Kimmeridgian transition (Zuo et al. 2018). However, due to limited biostratigraphic and chemostratigraphic data, as well as due to strong small-scale depositional variability, it remains challenging to correlate core and outcrop data of the Korallenoolith Fm. In order to address this problem, a carbon isotope-based framework has been established, which can be used to strengthen the existing biostratigraphic correlation scheme of the LSB.

The ostracod biostratigraphic zonation for the Korallenoolith Fm. is essentially based on previous studies. For the Eulenflucht-1 core, the zonation was developed by Heunisch and Luppold (2015). Based on the work of Schudack (1994) and Weiß (1995), Zuo et al. (2017) identified zones 6 to 10 in the upper part of the Bisperode section. Additionally, zones 7-14 could be assigned for the upper Langenberg section using new data (Zuo et al. (2017). However, the biostratigraphic zonation for the Lower and Middle Korallenoolith Fm. of both sections remains unclear. Regarding the Konrad #101 core, preliminary recognition of zones 3, and 6 to 12 was based on research by Kemper (1985) and Weiss (1985) (for further details see Chapter 3). In the Osterwald section, the ostracod zone 6 was recently identified (pers. com. J. Erbacher).

Based on the existing biostratigraphic framework and lithostratigraphic constraints, chemostratigraphic segments can be defined and correlated among the different sections across the studied area (Fig. 8). Based on a comparative analysis, the carbon isotope curve covering the Korallenoolith Fm. is subdivided into five distinct units. The lowermost unit 1 is defined based on the lithological expression of the Callovian/Oxfordian transition, which is described as an erosional surface cutting into the offshore marine claystones of the Ornatenton Fm. (Mönnig 2006; Mönnig et al. 2018). The deposits underlying this surface are mainly composed of claystones with very low carbonate content. In the SE part of the basin, those fine-grain offshore deposits are directly overlain by the shallow-marine Korallenoolith limestones (Mönnig 1989; Fischer 1991). Unit 2 includes the Heersum Fm. and the Lower Korallenoolith Fm. (Helm et al. 2003; Betzler et al. 2007; Bai et al. 2017) and is characterized by a distinct $\delta^{13}C$ positive shift followed by a rapid $\delta^{13}C$ decrease in the upper Lower Korallenoolith Fm. This positive carbon isotope excursion represents an important chemostratigraphic indicator for the inter-basinal correlation of the Lower Korallenoolith Fm. and is considered to be synchronous with the globally recorded Middle Oxfordian carbon isotope excursion (MOxE) (Jenkyns 1996; Weissert and Mohr 1996; Padden et al. 2001, 2002; Rais et al. 2007; Louis-Schmid et al. 2007; O'Dogherty et al. 2018; Eltom et al. 2018; Carmeille et al. 2020; Eldrett 2022) (for discussion see Chapter 3). In the study area, this positive carbon isotope shift is well expressed in the Konrad #101 core and, though less pronounced, in the Eulenflucht core and Osterwald section. Unit 3 is characterised by an overall negative $\delta^{13}C$ trend overlying the positive MOxE, which varies in amplitude and shape. In the more W' part of the basin, this interval is characterized by the appearance of a coral-rich boundstone interval. Based on rare and poorly preserved ammonite findings, this interval can be placed within the *variocostatus* subzone (for discussion see Helm et al. 2003c). At Osterwald, the coral-rich interval can be placed within the ostracod

zone 6 (pers. com. J. Erbacher). In the Konrad #101 core, unit 3 corresponds to two negative shifts in the $\delta^{13}C$ trend separated by a small positive bulge, which encompasses the transition from the Lower to Middle Korallenoolith Fm. This interval is placed within the lower ostracod zone 6 (Kemper, E. 1985; Weiss, W. 1985). The spatial occurrence of coral reef facies appears to be mainly controlled by local small-scale tectonic movements (Mönnig 2005) with this type of facies being restricted to the western part of the southern LSB. In the southeastern part of the basin, coral reef facies is replaced by other shallow-marine carbonate deposits (marls and oolitic limestones). Within unit 3, the $\delta^{13}C$ trend shows more fluctuations compared to the upper part of Korallenoolith Fm., but still enables a tentative correlation. Unit 4 is defined based on the occurrence of a pronounced emersion surface at its base, which is well-recognized in an increase in quartz content and peaks in gamma-ray logs (Kästner et al. 2008). This sequence boundary can be observed in other European basins during Oxfordian times (e.g., Gygi et al. 1998, Jacquin et al. 1998; Kästner et al. 2008). Above this unconformity, the carbon isotope record shows a relatively stable trend forming a plateau, which is terminated by a distinct negative shift. This interval of stable $\delta^{13}C$ values covers large parts of ostracod zone 6 and can be well correlated between the Bisperode section, Konrad #101 and Eulenflucht cores. Unit 5 is defined based on the existing correlation proposed by Zuo et al. (2018), who used ostracods and $^{87}Sr/^{86}Sr$ ratios to place this interval into the Süntel Fm. of the Lower Kimmeridgian (for Bisperode and Langenberg). For Konrad #101 core this interval is placed within the lower ostracod zone 7-12 (Kemper, E. 1985; Weiss, W. 1985) and with a similar carbon-isotopic trend to Eulenfucht-1 core and Bisperode, proposes a time-equivalent of Late Kimmeridgian. Within this interval, the $\delta^{13}C$ curve shows a bit of fluctuation, overall shows a relatively decreasing $\delta^{13}C$ tendency, which is comparable to the Oxfordian-Kimmeridgian boundary has also been reported from the Polish Jura Chain and the Swabian Alb in SW Germany (Wierzbowski, 2015). In summary, the combined geochemical and biostratigraphic data enable a tentative stratigraphic correlation of the Korallenoolith Fm. across the southern margin of the LSB. However, some differences and deviations are also observed, and further investigations are needed to better constrain the stratigraphic position and sedimentary expression of the Oxfordian strata within the studied section.
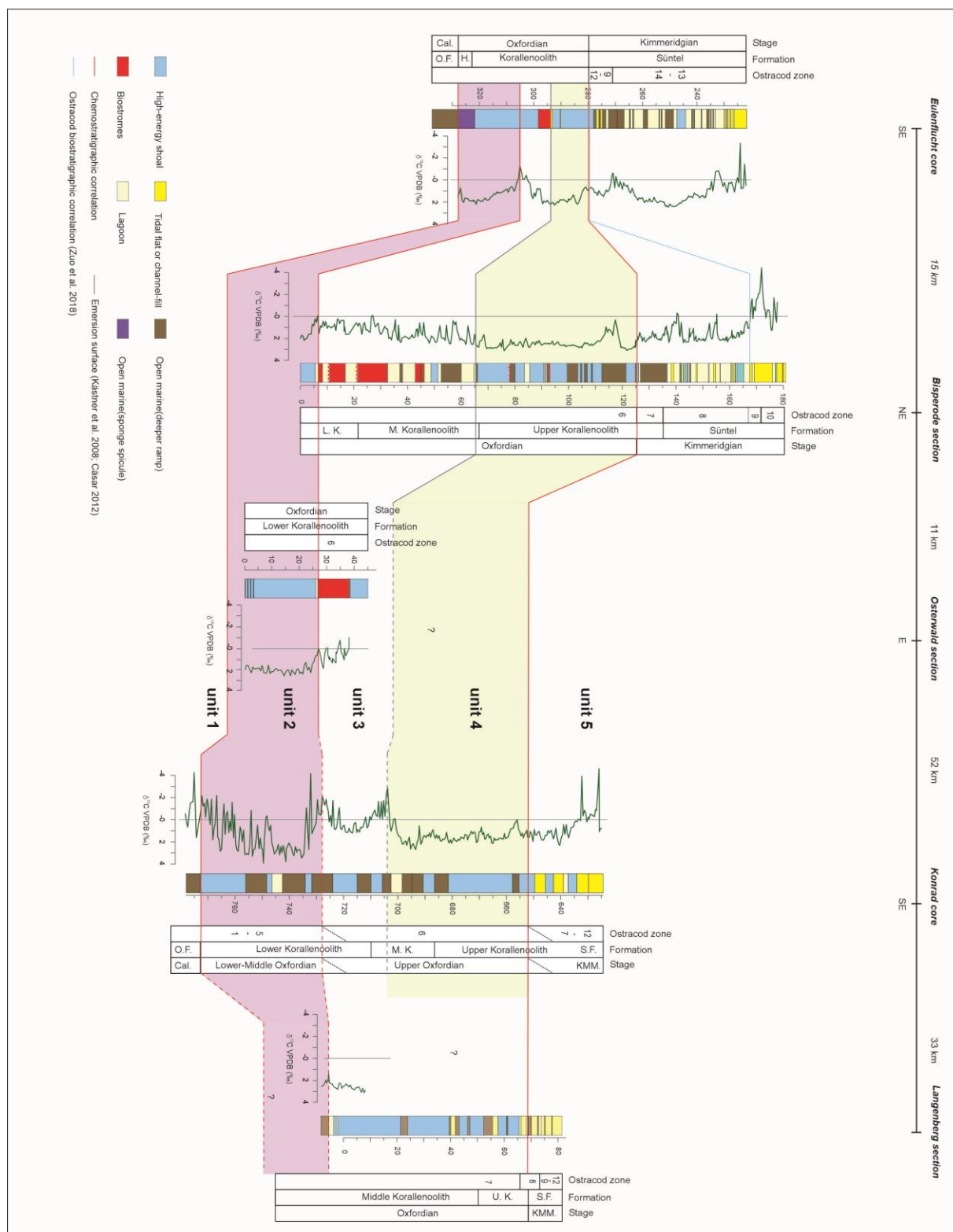
Fig. 8. Chemostratigraphic correlation based on carbon isotope trends across the southern LBS. For each section, lithostratigraphy, ostracod zonation, height, depositional setting and carbon isotope stratigraphic trends are shown. Correlation lines are based on chemostratigraphic (red), sedimentological (grey) and biostratigraphic (blue) constraints. The δ¹³C record of the Eulenflucht core is based on Bai et al. (2017), and the upper part of the Bisperode section (125 m–180 m) is based on Zuo et al. (2018).

5.8 Conclusions

This study provides detailed lithological logs of three Upper Jurassic sections (Bisperode, Osterwald, Langenberg) located in the LSB in northern Germany. While open-marine marker fossils, such as ammonites, are rare in the Oxfordian strata of the LSB, precise age assignment and correlation of the studied sections can be achieved using ostracod biostratigraphy. Chemostratigraphy, specifically the use of carbon isotopes, proved to be a valid and practical approach for regional correlation within the LSB, especially in the Korallenoolith Fm. where age-diagnostic fossils are scarce. A high-resolution study using carbon isotopes was conducted for the first time to correlate the different Oxfordian sections in the LSB. The observed $\delta^{13}C$ pattern between sections, even in the rather shallow-marine environments, was consistent, allowing for the establishment of a high-resolution carbon isotope stratigraphic record for Oxfordian successions in the LSB.

5.9 Acknowledgements

5.10 References

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6. Conclusions

This study focuses on refining the depositional setting and stratigraphy of the limestones of the Oxfordian Korallenoolith Fm. within the LSB. In order to achieve such a goal, an integrated approach combining sedimentological, sequence stratigraphic, biostratigraphic, and chemostratigraphic analysis has been applied to several Oxfordian sections and one scientific drill core. The major results of the current thesis include the following:

Analysis of the carbonate microfacies and establishment of a sequence stratigraphic framework

A total of seven superordinate carbonate facies types - composed of 14 different microfacies types - were distinguished throughout the Bisperode section and attributed to different paleoenvironments. Based on these findings a homoclinal ramp setting composed of different juxtaposed facies belts, ranging from semi-open lagoonal to open marine settings, is reconstructed. On the basis of microfacies types, diagnostic bedding surfaces, and the vertical lithofacies stacking pattern, a total of 15 small-, 8 medium-, and 3 large-scale sequences are identified. Detailed facies analysis and sequence stacking pattern of the Bisperode section suggest that eustatic fluctuations might have controlled the medium- and large-scale sequences preserved within the Korallenoolith Fm. based on their good match with well-established eustatic models (e.g., Hardenbol, 1998). Regional synsedimentary salt tectonism and sedimentation rate fluctuations may have played an additional role in relative sea-level changes within the LSB and as such influenced most of the small-scale sequences. Although it is clear that the lack of strong biostratigraphic markers limits the significance the correlation between regional and global sequence-stratigraphic schemes in the LSB, this work provides a general framework, which will help to better understand the link between the stacking pattern of Oxfordian strata in the LSB and allocyclic processes providing support for future chemo- and sequence-stratigraphic correlations.

First record of the Middle Oxfordian positive CIE within the Korallenoolith Formation

A new high-resolution inorganic δ^{13}C record illustrating a pronounced variation in the carbon isotope trend, which is obtained from a scientific borehole (Konrad #101 core) located in the LSB. Our δ^{13}C record is the first record of the Middle Oxfordian positive CIE within the LSB and is interpreted to reflect global δ^{13}C changes in ocean-atmosphere system. The positive CIE observed in the Konrad #101 core is an important chemostratigraphic marker for the inter-basinal correlation of the Lower Korallenoolith Fm. and considered to be synchronous with the globally recorded Middle Oxfordian carbon isotope excursion (MOxE). Our dataset, which is supported by well-defined tie points, further proves the usefulness of isotope variations recorded in shallow-water bulk carbonates as chemostratigraphic proxy.

^{87}Sr/^{86}Sr chemostratigraphy of Oxfordian shallow-water carbonate deposits

New biocalcite-derived ^{87}Sr/^{86}Sr data from the Oxfordian Korallenoolith Fm. from the LSB are used to identify secular trends in seawater Sr ratios in order to better constrain the depositional age of the Korallenoolith Fm. Sr isotope ratios obtained from brachiopod, oyster and trichites shell calcite are within the range of values reported for Late Jurassic seawater. However, closer inspection shows distinct deviations from the Oxfordian open marine Sr isotope signature, indicating that the depositional setting

was probably influenced by freshwater input with a continental Sr isotope signature. The analyzed shells may have captured local, more radiogenic $^{87}Sr/^{86}Sr$ signatures derived from riverine waters and hence failed to provide a more precise age assignment. Our $^{87}Sr/^{86}Sr$ results indicate that shells from shallow marine settings showing no diagenetic overprint can still deviate from the open marine Sr isotope signature.

High-resolution carbon isotope stratigraphic records for Oxfordian successions in the LSB

High-resolution $\delta^{13}C$ analysis of bulk carbonate samples from three outcrop sections (Langenberg, Osterwald, and Bisperode) and one scientific borehole (Konrad #101 core) are studied and compared. Through the application of rigorous criteria, the majority of the $\delta^{13}C$ dataset of bulk carbonate obtained from the studied sections has been deemed free from diagenetic alterations and local environmental effects, thereby providing a representation of the global marine signals. Based on litho- and biostratigraphic constraints, a $\delta^{13}C$ record correlation is presented for the southern LSB for the Oxfordian interval. Chemostratigraphy, specifically the use of carbon isotopes, proved to be a valid and practical approach for regional correlation within the LSB, especially in the Korallenoolith Fm. where age-diagnostic fossils are scarce. The chemostratigraphic data presented in this study enables the refinement of the pre-existing biostratigraphic framework and the establishment of a composite high-resolution $\delta^{13}C$ stratigraphic record. The $\delta^{13}C$ records improve the correlation ability between the western and eastern parts of the LSB. Overall, the new framework also allows to better assess the impact of carbon cycle disturbances on the shallow-marine carbonate systems in the LSB.

Appendix

Appendix 1 High-resolution log description of the Bisperode section (0–126 m)
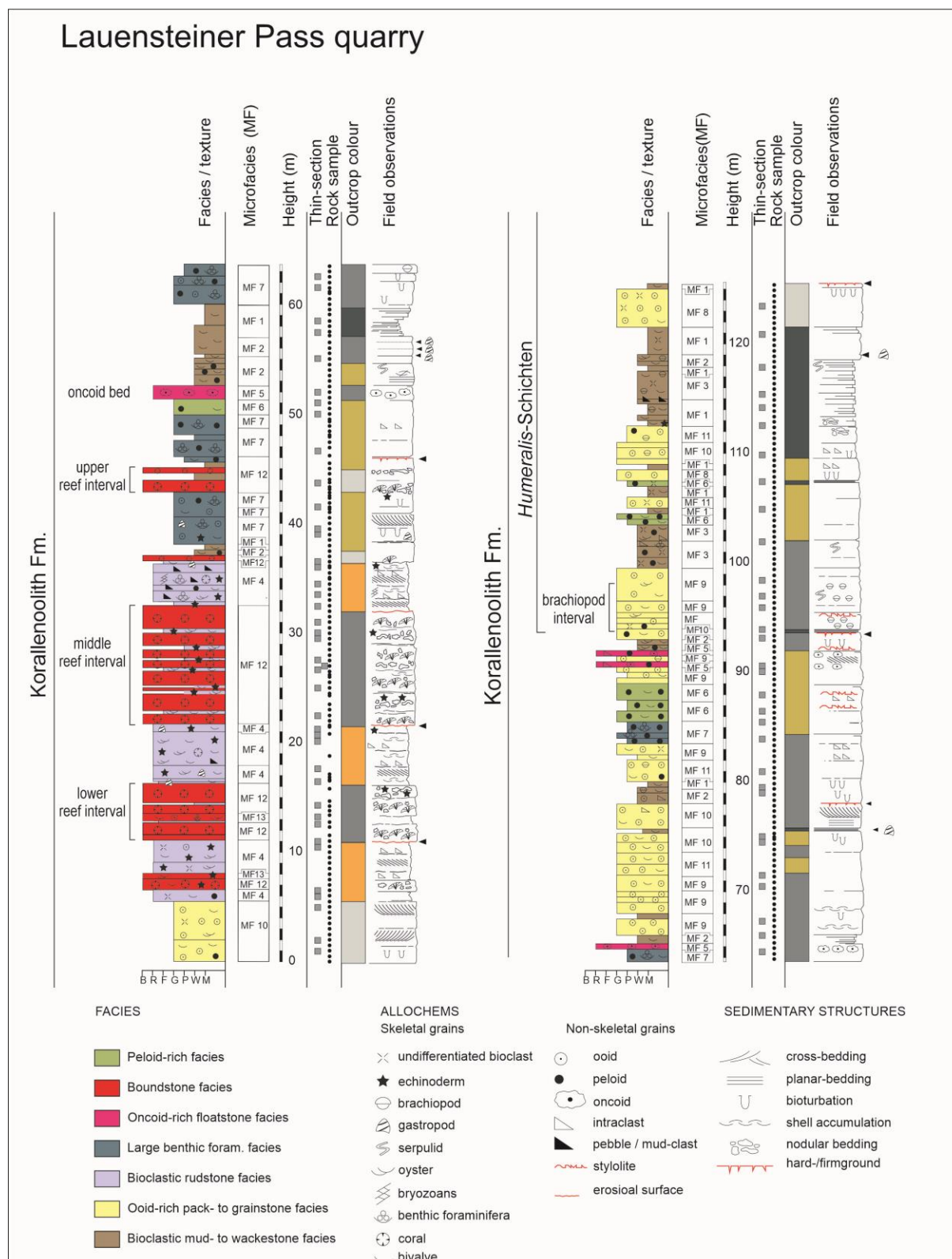
Appendix 2 Sedimentological description, depositional settings and sequence stratigraphic interpretation of the Bisperode section
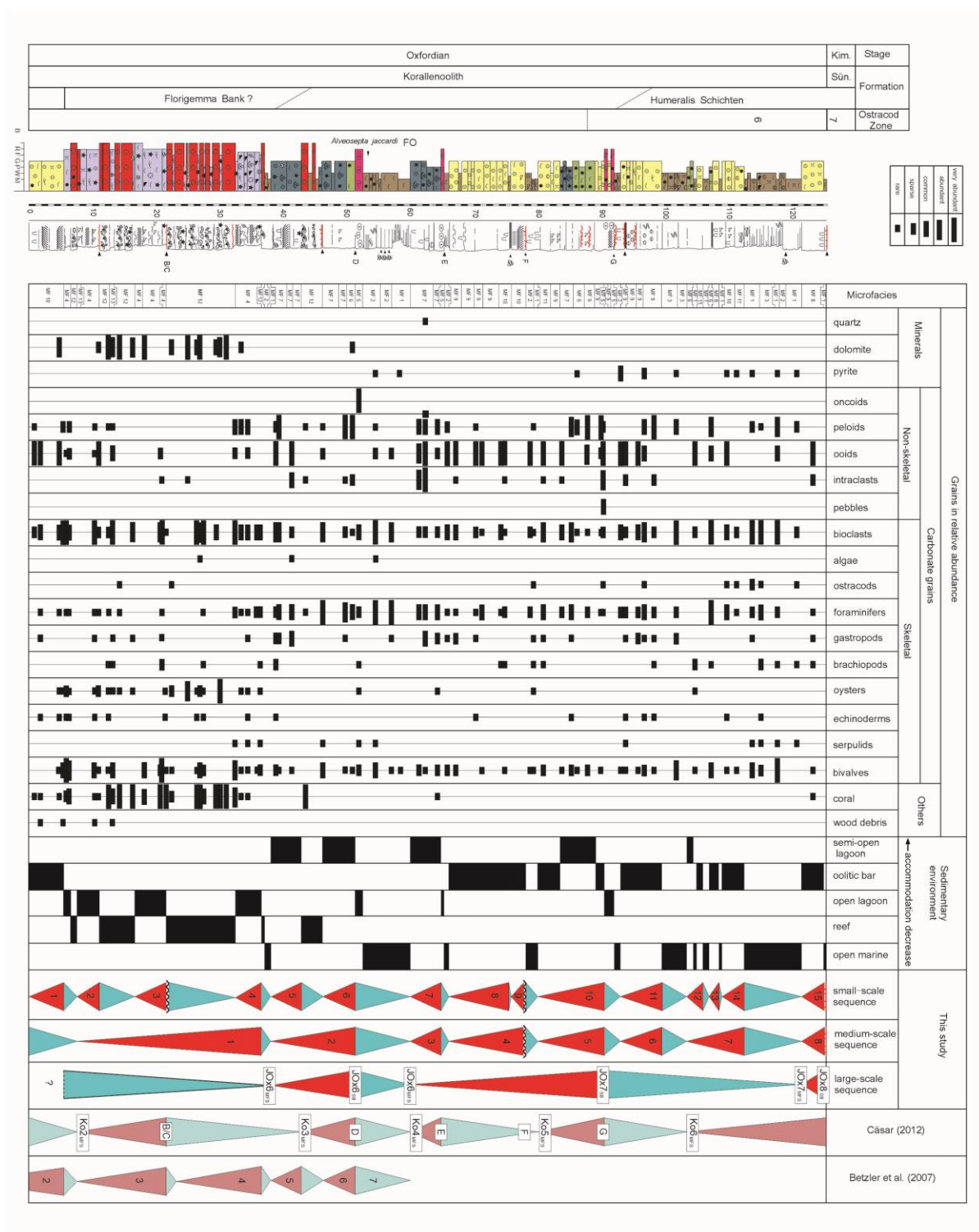
Appendix 3 Lithostratigraphy and high-resolution stable isotope stratigraphy (δ¹⁸O, δ¹³C) of the Konrad #101 core
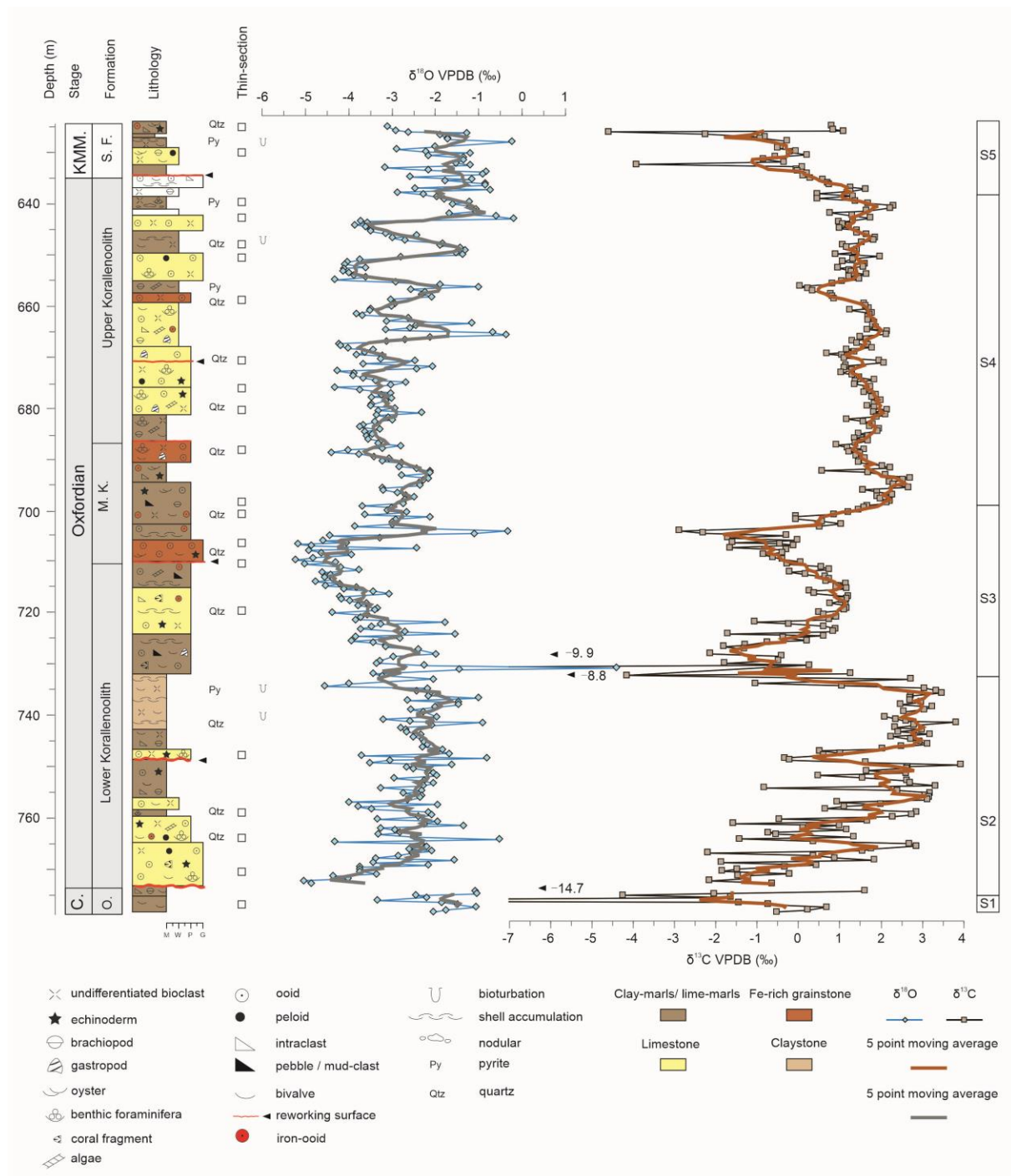
Appendix

Appendix 4 Lithostratigraphy, high-resolution stable isotope stratigraphy (δ¹⁸O, δ¹³C) and inferred depositional settings of the Bisperode section (0–126 m)
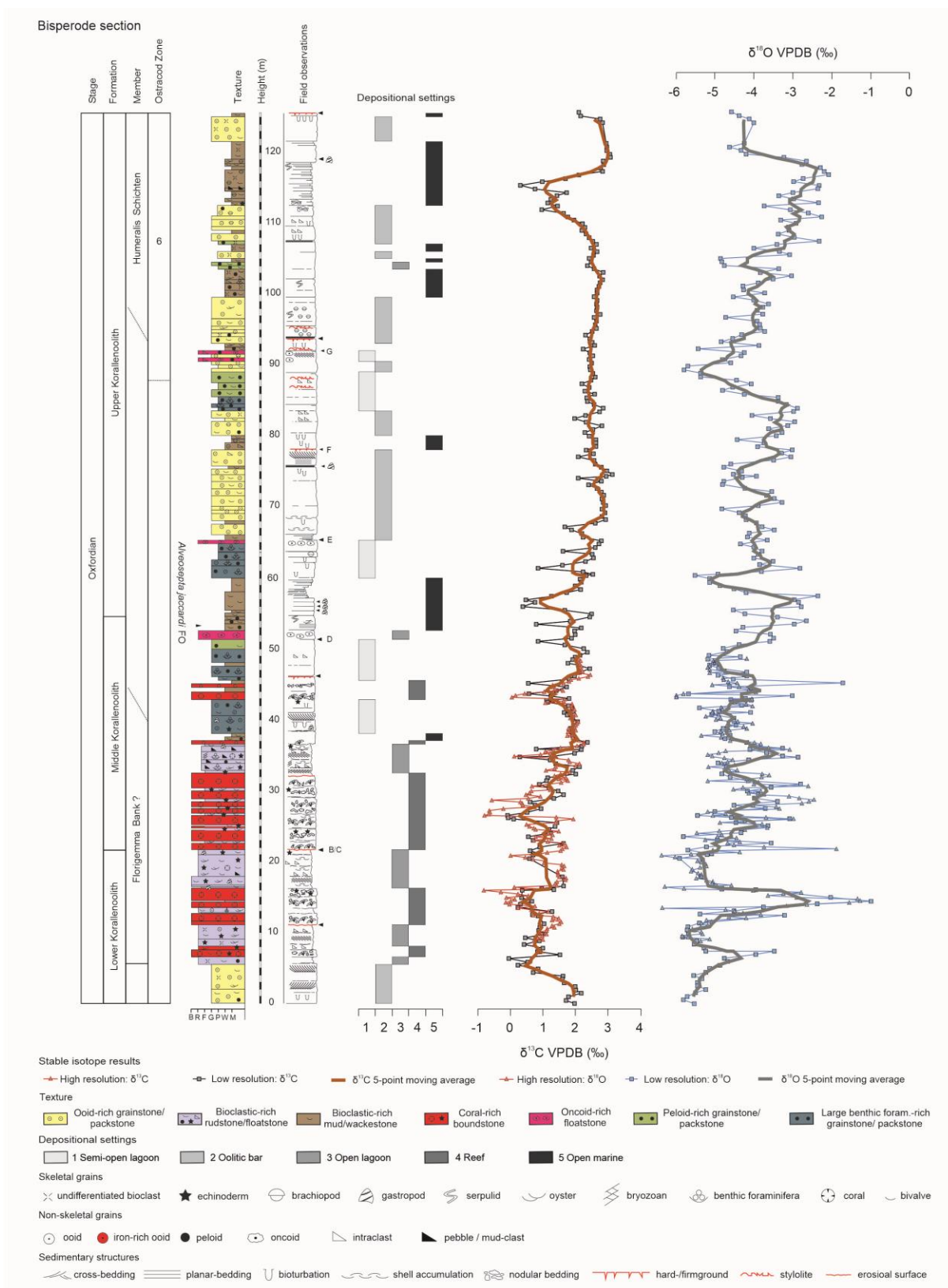
Appendix 5 Lithostratigraphy, inferred depositional settings and high-resolution stable isotope stratigraphy (δ¹⁸O, δ¹³C) of Osterwald section (0–46 m)
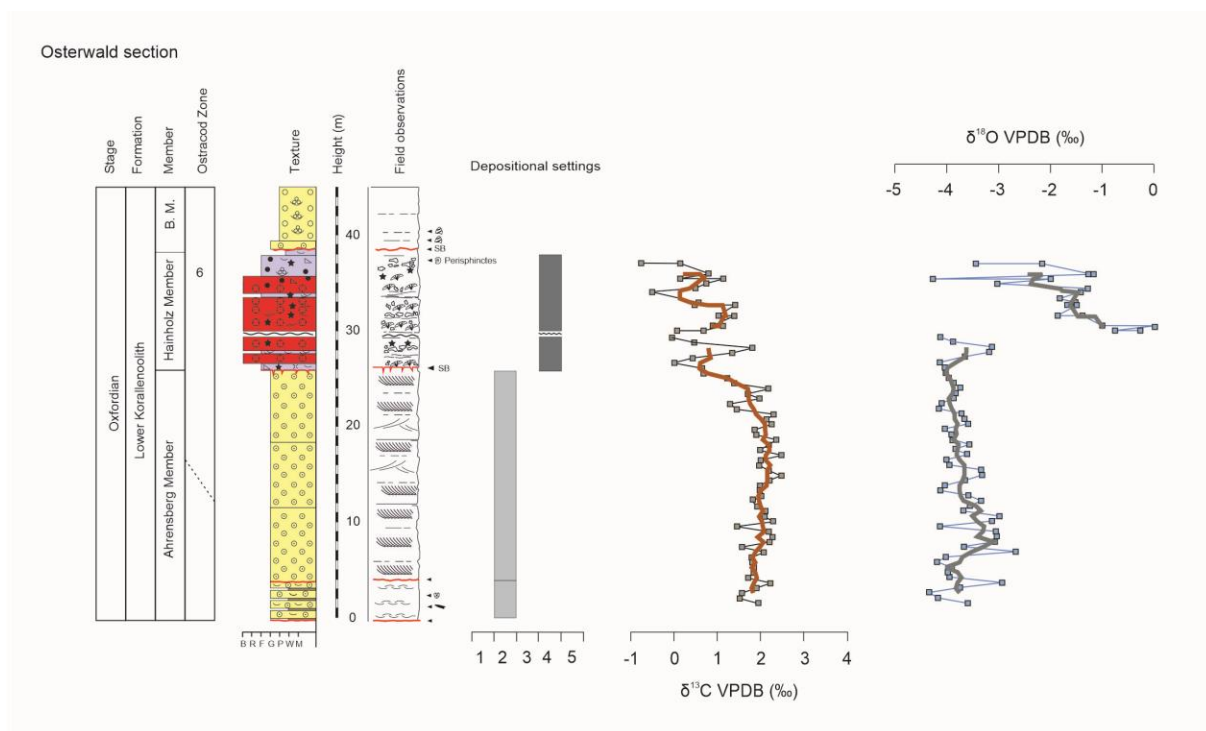
Appendix 6 Lithostratigraphy, inferred depositional settings and high-resolution stable isotope stratigraphy (δ¹⁸O, δ¹³C) of Langenberg section (0–16 m)
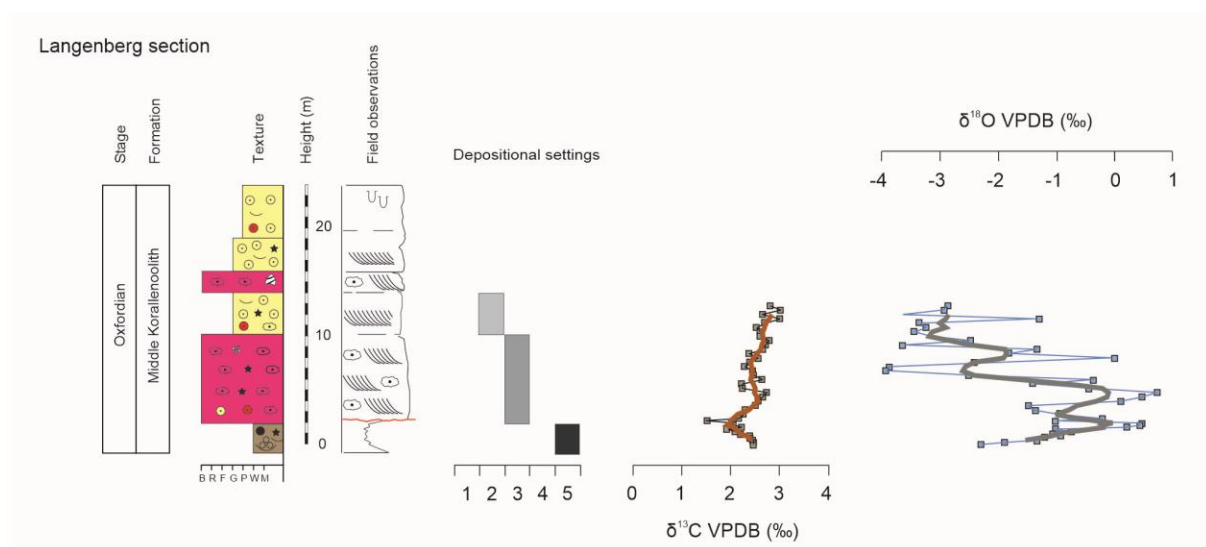
Appendix

Appendix 7 Lithostratigraphy versus $^{87}Sr/^{86}Sr$ ratios of selected calcite shell materials for (A)Bisperode section and (B) Konrad #101 core
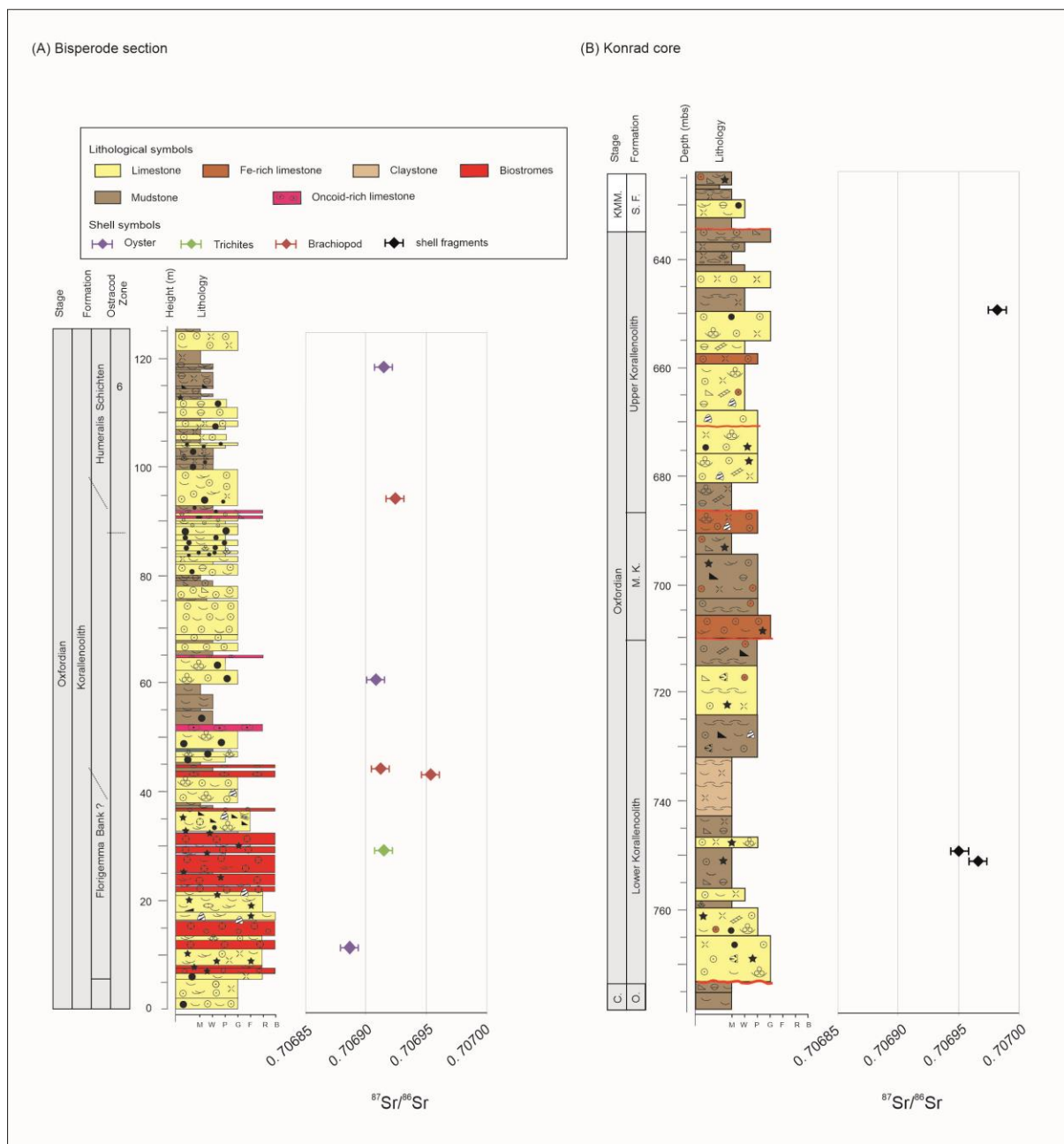
Appendix 8 Carbon and oxygen isotope results of bulk material, Bisperode section

Sample	Depth (m)	δ13C VPDB	s.d.	δ18O VPDB	s.d.	Sample	Depth (m)	δ13C VPDB	s.d.	δ18O VPDB	s.d.
DY0	0.00	1.98	0.08	-5.53	0.06	LPb 5,2	26.70	-0.06	0.06	-4.57	0.04
DY0_5	0.50	1.70	0.06	-5.81	0.04	LPb 5,5	27.00	-0.08	0.05	-5.45	0.02
DY1	1.00	1.79	0.09	-5.72	0.04	LPb 6	27.50	0.51	0.06	-5.01	0.05
DY1_5	1.50	2.17	0.06	-5.51	0.03	LPb 6,5	28.00	0.94	0.09	-3.71	0.07
DY2	2.00	2.01	0.06	-5.23	0.05	LPb 7	28.50	0.75	0.04	-4.52	0.04
DY2_5	2.50	1.99	0.09	-5.45	0.06	LPb 7,5	29.00	0.61	0.07	-3.39	0.07
DY3	3.00	1.65	0.08	-5.44	0.06	LPb 8	29.50	1.33	0.04	-3.98	0.03
DY3_5	3.50	1.60	0.06	-5.34	0.07	LPb 8,5	30.00	1.63	0.09	-3.88	0.07
DY4	4.00	1.61	0.11	-5.55	0.05	LPb 9	30.50	1.46	0.04	-4.16	0.03
DY4_5	4.50	0.70	0.07	-5.24	0.07	LPb 9,5	31.00	1.18	0.07	-3.56	0.07
DY5	5.00	0.85	0.05	-5.14	0.03	LPb 10	31.50	0.89	0.07	-2.81	0.03
DY5_5	5.50	0.23	0.09	-4.88	0.07	LPb 10,5	32.00	1.12	0.06	-4.16	0.05
DY6	6.00	0.53	0.09	-4.68	0.06	LPb 11	32.50	1.14	0.04	-4.61	0.01
DY6_5	6.50	-0.04	0.02	-4.75	0.02	LPb 11,5	33.00	2.01	0.05	-4.82	0.03
DY7	7.00	1.52	0.04	-3.95	0.05	LPb 12	33.50	1.91	0.04	-4.74	0.06
DY7_5__1	7.50	0.91	0.06	-3.47	0.03	LPb 12,5	34.00	2.13	0.06	-4.71	0.04
DY7_5__2	7.50	0.84	0.07	-5.24	0.05	LPb 13	34.50	1.38	0.07	-4.92	0.04
DY8	8.00	1.00	0.09	-5.28	0.10	LPb 13,5	35.00	1.23	0.05	-4.13	0.06
DY8_5	8.50	0.42	0.06	-5.53	0.06	LPb 13,9	35.40	0.30	0.06	-2.87	0.03
DY9	9.00	0.89	0.06	-5.47	0.05	LPb 14	35.50	1.29	0.05	-3.26	0.06
DY9_5	9.50	0.46	0.06	-5.83	0.05	LPb 14,5	36.00	1.97	0.04	-3.67	0.03
DY10	10.00	1.08	0.05	-5.67	0.04	LPb 15	36.50	2.17	0.06	-4.10	0.03
DY10_5	10.50	0.87	0.06	-5.71	0.04	SB 0	36.60	0.79	0.05	-3.26	0.07
DY11	11.00	0.91	0.07	-5.70	0.05	SB 0,5	37.00	2.19	0.08	-4.03	0.04
DY11_5	11.50	1.04	0.04	-5.40	0.05	SB 1	37.50	2.36	0.06	-4.19	0.03
LPa 1	12.65	0.84	0.09	-3.22	0.05	SB 1,5	38.00	1.95	0.05	-4.75	0.04
LPa 2	12.80	0.69	0.06	-5.38	0.01	SB 2	38.50	1.92	0.05	-4.61	0.04
LPa 3	13.25	1.27	0.05	-4.51	0.02	SB 2,5	39.00	1.80	0.05	-5.01	0.04
LPa 4	13.85	0.23	0.05	-3.76	0.01	SB 3	39.50	1.85	0.06	-4.79	0.03
LPa 5	14.30	0.31	0.08	-2.37	0.07	SB 3,5	40.00	1.94	0.08	-4.46	0.08
LPa 6	14.70	0.66	0.09	-0.98	0.03	SB 4	40.50	2.06	0.07	-4.51	0.06
LPa 7	15.20	0.35	0.07	-2.02	0.06	SB 4,5	41.00	1.91	0.03	-4.51	0.04
LPa 8	16.30	0.37	0.08	-3.95	0.06	SB 5	41.50	1.75	0.07	-5.09	0.05
LPa 9	16.40	1.34	0.05	-4.83	0.07	SB 5,3	41.80	1.65	0.02	-4.08	0.02
LPa 10	16.55	0.97	0.04	-4.83	0.03	SB 5,5	42.00	1.94	0.05	-4.90	0.04
LPa 11	16.90	1.63	0.06	-4.99	0.04	SB 5,9	42.40	1.90	0.03	-5.41	0.03
LPa 12	18.20	1.60	0.02	-5.36	0.06	SB 6,3	42.80	1.79	0.05	-4.32	0.06
LPa 13	20.80	0.58	0.05	-5.90	0.04	SB 6,8	43.30	1.15	0.07	-4.57	0.06
LPa 14	21.40	0.70	0.09	-5.20	0.06	SB 7,0	43.50	1.30	0.09	-4.07	0.09
LPb 0	21.50	0.88	0.03	-5.08	0.02	SB 7,1	43.60	1.12	0.06	-4.60	0.07
LPb 0, 5	22.00	0.62	0.02	-5.70	0.02	SB 7,3	43.80	1.79	0.03	-4.22	0.03
LPb 1	22.50	0.90	0.05	-5.22	0.06	SB 7,7	44.20	1.24	0.05	-3.01	0.04
LPb 1, 5	23.00	1.63	0.04	-3.56	0.02	SB 8	44.50	0.58	0.03	-5.69	0.04
LPb 2	23.50	0.70	0.07	-4.94	0.05	SB 8,5	45.00	1.42	0.09	-4.09	0.05
LPb 2, 5	24.00	0.55	0.09	-5.82	0.05	SB 9,0	45.50	1.72	0.08	-4.62	0.06
LPb 3, 3	24.50	1.24	0.03	-4.33	0.05	SB 9,5	46.00	0.55	0.09	-1.71	0.06
LPb 3, 5	25.00	1.18	0.04	-4.31	0.04	SB 10,1	46.60	1.81	0.07	-4.53	0.06
LPb 4	25.50	1.37	0.08	-3.65	0.07	SB 10,6	47.10	1.97	0.07	-4.92	0.05
LPb 4, 5	26.00	1.43	0.05	-4.47	0.06	SB 11,1	47.60	2.11	0.06	-4.18	0.04
LPb 5	26.50	0.11	0.04	-3.09	0.03	SB 11,6	48.10	2.43	0.08	-4.90	0.03

Appendix

Sample	Depth (m)	δ¹³C VPDB	s.d.	δ¹⁸O VPDB	s.d.	Sample	Depth (m)	δ¹³C VPDB	s.d.	δ¹⁸O VPDB	s.d.
SB 12,1	48.60	2.09	0.04	-5.14	0.02	SB 36_5	73	2.87	0.01	-3.67	0.05
SB 12,4	48.90	1.77	0.07	-4.99	0.04	SB 37_0	73.5	2.79	0.03	-3.54	0.04
SB 12,9	49.40	1.91	0.03	-5.19	0.05	SB 37_5	74	2.66	0.04	-4.23	0.06
SB 13,3	49.80	2.00	0.07	-4.35	0.04	SB 38_0	74.5	2.39	0.03	-4.81	0.03
SB 13_5	50.00	2.14	0.03	-5.15	0.08	SB 38_5	75	2.79	0.05	-4.77	0.03
SB 14_0	50.50	2.36	0.05	-4.7	0.04	SB 38_9	75.5	2.08	0.07	-4.30	0.03
SB 14_5	51.00	2.25	0.03	-4.79	0.07	SB 39_2	75.7	2.94	0.05	-3.93	0.02
SB 15_0	51.50	1.66	0.09	-4.39	0.04	SB 35_5	76	3.12	0.03	-4.53	0.02
SB 15_5	52.00	0.84	0.03	-3.6	0.04	SB 40_0	76.5	2.96	0.01	-4.32	0.07
SB 16_0	52.50	1.87	0.04	-3.5	0.03	SB 40_5	77	2.79	0.05	-4.77	0.03
SB 16_5	53.00	1.99	0.06	-3.57	0.04	SB 41_0	77.5	2.61	0.06	-4.60	0.05
SB 17_0	53.50	1.96	0.02	-4.47	0.05	SB 41_5	78	2.56	0.04	-3.49	0.03
SB17_5	54.00	2.18	0.04	-4.28	0.04	SB 42_0	78.5	2.09	0.03	-3.04	0.04
SB 18_0	54.50	0.8	0.08	-2.97	0.05	SB 42_5	79	2.54	0.03	-3.30	0.03
SB 18_4	54.90	1.84	0.07	-2.65	0.04	SB 43_0	79.5	2.32	0.06	-3.02	0.02
SB 19_0	55.50	2.43	0.07	-3.39	0.02	SB 43_5	80	2.62	0.05	-3.90	0.06
SB 19_5	56.00	2.48	0.11	-4.24	0.06	SB 44_0	80.5	2.63	0.04	-3.74	0.05
SB 20_0	56.50	1.68	0.03	-4.53	0.05	SB 44_5	81	2.63	0.06	-4.44	0.05
SB 20_5	57.00	0.39	0.05	-2.78	0.03	SB 45_0	81.5	2.42	0.06	-3.42	0.04
SB 21_1	57.60	0.75	0.06	-2.85	0.06	SB 45_5	82	2.28	0.05	-3.28	0.05
SB 21_5	58.00	0.48	0.02	-2.97	0.05	SB 46_0	82.5	2.53	0.04	-3.63	0.02
SB 22_0	58.50	1.27	0.08	-2.35	0.05	SB 46_5	83	2.80	0.09	-3.14	0.05
SB 22_5	59.00	1.73	0.07	-4.21	0.08	SB 47_0	83.5	2.33	0.04	-2.95	0.04
SB 23_0	59.5	2.16	0.11	-4.51	0.06	SB 47_5	84	1.97	0.06	-3.57	0.05
SB 23_5	60	1.99	0.06	-4.87	0.04	SB 48_0	84.5	2.30	0.06	-4.05	0.05
SB 24_0	60.5	2.17	0.02	-5.13	0.07	SB 48_5	85	2.73	0.04	-2.98	0.05
SB 24_5	61	2.14	0.06	-5.13	0.05	SB 49_0	85.5	2.84	0.05	-2.89	0.05
SB 25_0	61.5	2.33	0.02	-5.51	0.06	SB 49_5	86	2.56	0.04	-3.17	0.01
SB 25_2	61.7	2.53	0.05	-4.93	0.04	SB 50_0	86.5	2.36	0.03	-3.38	0.02
SB 25_5	62	2.23	0.05	-3.81	0.03	SB 50_5	87	2.35	0.04	-3.37	0.04
SB 26_0	62.5	0.85	0.04	-2.82	0.04	SB 51_0	87.5	2.58	0.01	-4.25	0.06
SB 26_5	63	1.59	0.07	-3.86	0.06	SB 51_5	88	2.28	0.06	-4.81	0.04
SB 27_0	63.5	2.30	0.02	-3.50	0.06	SB 52_0	88.5	2.43	0.03	-4.54	0.05
SB 27_5	64	2.54	0.04	-4.00	0.02	SB 52_5	89	2.18	0.05	-4.07	0.03
SB 28_0	64.5	2.51	0.04	-3.89	0.03	SB 53_0	89.5	2.48	0.07	-4.44	0.04
SB 28_5	65	1.62	0.05	-3.79	0.02	SB 53_5	90	2.60	0.04	-5.37	0.03
SB 29_0	65.5	2.61	0.03	-4.01	0.05	SB 54_0	90.5	2.53	0.04	-5.36	0.02
SB 29_5	66	2.72	0.03	-4.35	0.04	SB 54_5	91	2.45	0.04	-5.80	0.06
SB 30_0	66.5	2.79	0.05	-3.65	0.04	SB 55_0	91.5	2.44	0.06	-5.69	0.05
SB 30_5	67	2.23	0.07	-4.17	0.06	SB 55_5	92	2.48	0.05	-4.59	0.07
SB 31_0	67.5	2.19	0.04	-4.12	0.05	SB 56_0	92.5	2.43	0.05	-4.81	0.02
SB 31_5	68	1.89	0.03	-3.48	0.04	SB 56_5	93	2.52	0.05	-4.34	0.04
SB 32_0	68.5	1.67	0.03	-3.79	0.03	SB 57_0	93.5	2.44	0.04	-4.25	0.03
SB 32_5	69	2.60	0.07	-3.94	0.05	SB 57_5	94	2.24	0.03	-5.43	0.03
SB 33_0	69.5	2.92	0.08	-4.20	0.05	SB 58_0	94.5	2.58	0.05	-3.86	0.03
SB 33_5	70	2.81	0.05	-4.21	0.05	SB 58_5	95	2.52	0.02	-4.84	0.04
SB 34_0	70.5	2.90	0.06	-4.38	0.05	SB 59_0	95.5	2.43	0.05	-4.54	0.04
SB 34_5	71	2.81	0.03	-4.82	0.04	SB 59_5	96	2.30	0.07	-4.31	0.04
SB 35_0	71.5	2.93	0.04	-3.89	0.03	SB 60_0	96.5	2.51	0.05	-3.72	0.05
SB 35_5	72	2.86	0.04	-3.28	0.02	SB 60_5	97	2.63	0.06	-3.83	0.04
SB 36_0	72.5	2.82	0.08	-3.48	0.04	SB 61_0	97.5	2.61	0.03	-3.85	0.03

Sample	Depth (m)	δ¹³C VPDB	s.d.	δ¹⁸O VPDB	s.d.	Sample	Depth (m)	δ¹³C VPDB	s.d.	δ¹⁸O VPDB	s.d.
SB 61_5	98	2.65	0.02	-3.92	0.06	SB 87_0	123.5	2.93	0.02	-4.25	0.04
SB 62_0	98.5	2.57	0.04	-4.72	0.05	SB 87_5	126.5	2.82	0.04	-4.00	0.02
SB_62_5	99	2.75	0.06	-3.78	0.04	SB 88_0	127	2.75	0.06	-4.12	0.02
SB_63_0	99.5	2.65	0.06	-3.92	0.03	SB 88_5	127.5	2.16	0.05	-4.37	0.05
SB_63_5	100	2.65	0.03	-3.78	0.07	SB 89_0	128	2.11	0.03	-4.58	0.02
SB_64_0	100.5	2.63	0.05	-3.63	0.03						
SB_64_5	101	2.67	0.07	-4.01	0.03						
SB_65_0	101.5	2.57	0.03	-4.53	0.03						
SB_65_5	102	2.66	0.05	-3.73	0.04						
SB_66_0	102.5	2.66	0.05	-4.27	0.04						
SB_66_5	103	2.72	0.04	-4.28	0.02						
SB_67_0	103.5	2.75	0.05	-3.89	0.05						
SB_67_5	104	2.83	0.04	-3.50	0.04						
SB_68_0	104.5	2.73	0.02	-3.04	0.05						
SB_68_5	105	2.84	0.06	-3.84	0.03						
SB_69_0	105.5	2.57	0.05	-3.36	0.03						
SB_69_5	106	2.37	0.06	-4.77	0.02						
SB_70_0	106.5	2.48	0.05	-4.82	0.02						
SB_70_5	107	2.41	0.06	-4.86	0.04						
SB_71_0	107.5	2.55	0.03	-3.08	0.02						
SB_71_5	108	2.65	0.07	-3.34	0.03						
SB_72_0	108.5	2.48	0.03	-4.00	0.03						
SB_72_5	109	2.63	0.05	-3.41	0.03						
SB_73_0	109.5	2.52	0.06	-2.33	0.04						
SB_73_5	110	2.42	0.03	-2.96	0.03						
SB_74_0	110.5	2.32	0.05	-3.37	0.04						
SB_74_5	111	2.20	0.07	-3.10	0.03						
SB_75_0	111.5	2.28	0.06	-3.11	0.03						
SB_75_5	112	2.22	0.04	-2.92	0.04						
SB_76_0	112.5	1.96	0.02	-3.32	0.02						
SB_76_5	113	1.77	0.06	-2.26	0.03						
SB_77_0	113.5	1.64	0.08	-2.61	0.05						
SB_77_5	114	0.95	0.07	-3.06	0.04						
SB_78_0	114.5	1.44	0.02	-3.74	0.06						
SB_78_5	115	1.15	0.05	-2.34	0.05						
SB_79_0	115.5	1.25	0.02	-2.98	0.06						
SB_79_5	116	1.42	0.07	-3.37	0.04						
SB_80_0	116.5	1.73	0.05	-2.99	0.02						
SB_80_5	117	0.77	0.02	-2.35	0.03						
SB_81_0	117.5	0.31	0.07	-2.32	0.02						
SB_81_5	118	0.97	0.03	-2.98	0.04						
SB_82_0	118.5	1.69	0.04	-2.74	0.04						
SB 82_5	119	2.11	0.02	-2.08	0.06						
SB 83_0	119.5	2.83	0.04	-2.20	0.03						
SB 83_5	120	2.78	0.06	-2.30	0.04						
SB 84_0	120.5	2.87	0.06	-2.76	0.05						
SB 84_5	121	2.84	0.04	-2.65	0.04						
SB 85_0	121.5	3.06	0.06	-3.24	0.03						
SB 85_5	122	3.06	0.05	-4.19	0.04						
SB 86_0	122.5	2.96	0.07	-4.33	0.05						
SB 86_5	123	2.96	0.10	-4.62	0.05						

Appendix

Appendix 9 Carbon and oxygen isotope results of drilled powder, Bisperode section

Sample	Depth (m)	δ¹³C VPDB	s.d.	δ¹⁸O VPDB	s.d.	Sample	Depth (m)	δ¹³C VPDB	s.d.	δ¹⁸O VPDB	s.d.
SA_10_25	9	0.72	0.04	-5.37	0.04	SA 22_75	21.5	0.92	0.05	-5.62	0.04
SA_10_5	9.25	0.99	0.05	-5.13	0.03	SA 23_0	21.75	1.14	0.09	-4.37	0.02
SA_10_75	9.5	0.84	0.04	-5.70	0.03	SA 23_25	22	1.55	0.04	-5.06	0.04
SA_11_0	9.75	0.98	0.03	-5.85	0.03	SA 23_5	22.25	1.59	0.06	-1.87	0.04
SA_11_25	10	1.11	0.06	-5.32	0.02	SA 23_75	22.5	1.72	0.02	-3.74	0.05
SA_11_5	10.25	0.88	0.01	-5.35	0.06	SA 24_0	22.75	1.50	0.03	-4.52	0.03
SA_11_75	10.5	1.12	0.04	-5.54	0.03	SA 24_25	23	1.67	0.03	-4.68	0.02
SA_12_0	10.75	1.13	0.04	-5.59	0.02	SA 24_5	23.25	1.15	0.02	-4.37	0.04
SA_12_25	11	1.35	0.06	-5.37	0.03	SA 24_75	23.5	0.73	0.04	-5.26	0.03
SA_12_5	11.25	1.27	0.05	-5.19	0.05	SA 25_0	23.75	1.27	0.07	-4.45	0.05
SA_12_75	11.5	1.51	0.04	-5.35	0.03	SA 25_25	24	0.77	0.04	-4.93	0.04
SA_13_0	11.75	1.56	0.05	-5.09	0.04	SA 25_50	24.25	1.30	0.07	-4.82	0.04
SA_13_25	12	1.28	0.06	-5.22	0.04	SA 25_75	24.5	1.17	0.06	-5.46	0.05
SA_13_5	12.25	1.48	0.02	-4.19	0.08	SA 26_0	24.75	1.49	0.08	-4.88	0.06
SA_13_75	12.5	1.31	0.05	-4.65	0.05	SA 26_25	25	0.78	0.05	-4.24	0.04
SA_14_0	12.75	0.70	0.02	-3.81	0.05	SA 26_50	25.25	0.71	0.02	-3.66	0.04
SA_14_25	13	0.88	0.03	-4.28	0.03	SA 26_75	25.5	0.58	0.03	-3.99	0.03
SA_14_5	13.25	1.16	0.03	-4.50	0.04	SA 27_0	25.75	0.49	0.06	-3.78	0.03
SA_14_75	13.5	0.64	0.07	-4.72	0.04	SA 27_25	26	1.40	0.07	-4.88	0.07
SA_15_0	13.75	0.23	0.02	-6.36	0.06	SA 27_50	26.25	1.41	0.06	-4.23	0.02
SA_15_25	14	0.76	0.03	-3.16	0.06	SA 27_75	26.5	1.92	0.06	-2.98	0.03
SA_15_5	14.25	-0.03	0.07	-2.64	0.03	SA 28_0	26.75	1.41	0.04	-3.68	0.02
SA_15_75	14.5	-0.14	0.05	-1.56	0.05	SA 28_25	27	-0.79	0.05	-5.06	0.02
SA_16_0	14.75	0.01	0.06	-1.27	0.02	SA 28_5	27.25	-0.67	0.06	-4.73	0.04
SA_16_25	15	0.14	0.06	-1.33	0.04	SA 28_75	27.5	-0.63	0.06	-5.19	0.03
SA_16_5	15.25	-0.11	0.04	-2.89	0.04	SA 29_0	27.75	-0.65	0.07	-4.60	0.05
SA_16_75	15.5	0.55	0.06	-3.64	0.05	SA 29_25	28	-0.21	0.05	-3.35	0.03
SA_17_0	15.75	0.23	0.02	-3.24	0.06	SA 29_5	28.25	0.74	0.04	-3.43	0.04
SA_17_25	16	-0.28	0.03	-2.78	0.03	SA 29_75	28.5	0.38	0.04	-4.03	0.03
SA_17_5	16.25	-0.80	0.05	-4.02	0.02	SA 30_0	28.75	0.37	0.01	-2.77	0.05
SA_17_75	16.5	0.94	0.08	-5.79	0.04	SA 30_25	29	0.32	0.06	-2.59	0.03
SA_18_0	16.75	0.13	0.03	-6.28	0.02	SA 30_5	29.25	-0.57	0.06	-2.45	0.03
SA_18_25	17	1.43	0.07	-4.58	0.03	SA 30_75	29.5	0.56	0.04	-2.84	0.04
SA_18_5	17.25	1.37	0.04	-5.07	0.03	SA 31_0	29.75	0.92	0.03	-3.10	0.05
SA_18_75	17.5	1.43	0.05	-5.05	0.04	SA 31_25	30	0.48	0.05	-3.73	0.04
SA_19_0	17.75	1.70	0.04	-5.22	0.04	SA 31_5	30.25	0.59	0.06	-4.14	0.04
SA_19_25	18	1.71	0.06	-5.48	0.03	SA 31_75	30.5	0.65	0.06	-3.83	0.04
SA_19_5	18.25	1.50	0.03	-5.35	0.06	SA 32_0	30.75	1.22	0.03	-4.53	0.05
SA_19_75	18.5	1.46	0.04	-5.34	0.03	SA 32_25	31	1.26	0.04	-4.29	0.05
SA_20_0	18.75	1.46	0.04	-5.44	0.01	SA 32_5	31.25	0.65	0.05	-2.61	0.06
SA_20_25	19	1.45	0.02	-5.62	0.03	SA 32_75	31.5	1.17	0.07	-4.01	0.02
SA_20_5	19.25	1.64	0.03	-5.58	0.02	SA 33_0	31.75	1.56	0.08	-3.89	0.04
SA_20_75	19.5	1.58	0.03	-5.39	0.03	SA 33_25	32	1.77	0.04	-5.18	0.05
SA_21_0	19.75	1.65	0.06	-5.22	0.05	SA 33_5	32.25	1.48	0.05	-4.19	0.05
SA_21_25	20	1.59	0.07	-5.23	0.04	SA 33_75	32.5	1.71	0.04	-3.80	0.03
SA_21_5	20.25	1.04	0.06	-5.35	0.03	SA 34_0	32.75	1.36	0.05	-3.60	0.04
SA_21_75	20.5	1.05	0.05	-5.45	0.04	SA 34_25	33	1.54	0.05	-3.79	0.03
SA_22_0	20.75	0.70	0.03	-5.32	0.03	SA 34_5	33.25	1.82	0.02	-4.62	0.04
SA_22_25	21	0.47	0.04	-6.02	0.03	SA 34_75	33.5	1.09	0.04	-4.44	0.03
SA_22_5	21.25	0.01	0.05	-6.37	0.03	SA 35_0	33.75	1.35	0.07	-4.67	0.06

Sample	Depth (m)	δ¹³C VPDB	s.d.	δ¹⁸O VPDB	s.d.	Sample	Depth (m)	δ¹³C VPDB	s.d.	δ¹⁸O VPDB	s.d.
SA 35_25	34	1.39	0.07	-5.17	0.04	SA 48_0	46.75	2.11	0.04	-4.79	0.04
SA 35_5	34.25	2.00	0.04	-4.50	0.02	SA 48_25	47	2.37	0.04	-4.18	0.04
SA 35_75	34.5	2.13	0.08	-4.83	0.07	SA 48_50	47.25	2.45	0.06	-4.25	0.04
SA 36_0	34.75	1.83	0.03	-4.68	0.01	SA 48_75	47.5	2.06	0.02	-5.13	0.02
SA 36_25	35	1.78	0.05	-4.55	0.01	SA 49_0	47.75	2.21	0.03	-4.72	0.03
SA 36_5	35.25	1.31	0.07	-4.75	0.04	SA 49_25	48	2.10	0.07	-5.14	0.05
SA 36_75	35.5	0.12	0.05	-5.08	0.04	SA 49_50	48.25	2.13	0.03	-5.19	0.03
SA 37_0	35.75	0.92	0.05	-5.19	0.04	SA 49_75	48.5	2.17	0.07	-5.14	0.03
SA 37_25	36	1.23	0.07	-4.91	0.05	SA 50_0	48.75	2.13	0.07	-4.90	0.05
SA 37_5	36.25	1.07	0.06	-4.73	0.03	SA 50_25	49	2.10	0.06	-5.02	0.03
SA 37_75	36.5	1.32	0.09	-3.09	0.03	SA 50_50	49.25	2.15	0.04	-5.03	0.04
SA 38_0	36.75	1.54	0.08	-3.62	0.04	SA 50_75	49.5	2.10	0.06	-4.18	0.04
SA 38_25	37	2.05	0.09	-4.10	0.05						
SA 38_5	37.25	2.26	0.03	-3.82	0.03						
SA 38_75	37.5	2.25	0.05	-3.99	0.04						
SA 39_0	37.75	1.90	0.03	-4.61	0.02						
SA 39_25	38	2.02	0.03	-4.58	0.04						
SA 39_5	38.25	1.92	0.04	-4.83	0.05						
SA 39_75	38.5	1.75	0.05	-5.35	0.05						
SA 40_0	38.75	1.97	0.02	-4.81	0.05						
SA 40_25	39	1.77	0.06	-4.86	0.03						
SA 40_5	39.25	2.00	0.02	-4.64	0.05						
SA 40_75	39.5	1.78	0.06	-4.19	0.05						
SA 41_0	39.75	1.97	0.05	-4.27	0.04						
SA 41_25	40	2.00	0.09	-4.69	0.05						
SA 41_5	40.25	2.05	0.05	-4.03	0.03						
SA 41_75	40.5	2.08	0.06	-4.42	0.03						
SA 42_0	40.75	1.92	0.07	-4.97	0.05						
SA 42_25	41	1.84	0.03	-4.87	0.03						
SA 42_5	41.25	1.92	0.02	-5.23	0.03						
SA 42_75	41.5	2.01	0.04	-4.91	0.04						
SA 43_0	41.75	1.83	0.05	-5.07	0.04						
SA 43_25	42	1.84	0.04	-5.06	0.04						
SA 43_50	42.25	1.96	0.06	-4.81	0.05						
SA 43_75	42.5	1.89	0.03	-4.85	0.05						
SA 44_0	42.75	1.87	0.06	-4.04	0.06						
SA 44_25	43	1.89	0.06	-4.19	0.04						
SA 44_50	43.25	1.07	0.05	-4.50	0.05						
SA 44_75	43.5	1.63	0.06	-4.21	0.02						
SA 45_0	43.75	1.68	0.06	-4.05	0.04						
SA 45_25	44	0.05	0.05	-5.99	0.03						
SA 45_50	44.25	0.15	0.02	-5.99	0.02						
SA 45_75	44.5	0.44	0.05	-5.81	0.04						
SA 46_0	44.75	1.03	0.04	-3.95	0.04						
SA 46_25	45	1.61	0.06	-4.13	0.06						
SA 46_50	45.25	1.38	0.02	-4.07	0.02						
SA 46_75	45.5	1.31	0.03	-4.38	0.02						
SA 47_0	45.75	1.30	0.06	-5.06	0.05						
SA 47_25	46	1.63	0.07	-4.42	0.04						
SA 47_50	46.25	1.80	0.08	-4.65	0.06						
SA 47_75	46.5	1.86	0.05	-4.78	0.07						

Appendix

Appendix 10 Carbon and oxygen isotope results of drilled powder, Konrad #101 core

Sample	Depth (m)	δ13C VPDB	s.d.	δ18O VPDB	s.d.	Sample	Depth (m)	δ13C VPDB	s.d.	δ18O VPDB	s.d.
K_624_96	624.96	0.80	0.09	-3.10	0.06	K_646_99	646.99	1.82	0.07	-2.70	0.03
K_625_46	625.46	0.84	0.08	-2.91	0.03	K_647_49	647.49	1.53	0.09	-1.83	0.07
K_625_77	625.77	1.09	0.05	-2.62	0.02	K_647_93	647.93	1.06	0.11	-1.88	0.07
K_625_90	625.90	-4.60	0.03	-1.26	0.06	K_648_43	648.43	1.16	0.02	-1.42	0.04
K_626_37	626.37	2.25	0.06	-1.89	0.07	K_648_86	648.86	1.41	0.09	-1.30	0.05
K_626_87	626.87	0.81	0.11	-1.71	0.06	K_649_36	649.36	1.37	0.06	-1.50	0.05
K_627_15	627.15	0.93	0.07	-1.70	0.05	K_649_76	649.76	0.90	0.07	-1.35	0.07
K_627_65	627.65	0.28	0.08	-0.22	0.06	K_650_26	650.26	1.97	0.06	-2.79	0.03
K_628_16	628.16					K_650_72	650.72	1.31	0.09	-3.74	0.06
K_628_66	628.66	-0.44	0.03	-1.99	0.04	K_651_22	651.22	1.06	0.03	-4.03	0.03
K_629_08	629.08	-0.51	0.05	-2.88	0.06	K_651_64	651.64	1.60	0.03	-4.09	0.03
K_629_58	629.58	-0.06	0.05	-2.21	0.05	K_652_25	652.25	1.57	0.04	-3.61	0.03
K_629_85	629.85	-0.21	0.08	-1.19	0.08	K_652_45	652.45	0.96	0.06	-4.11	0.02
K_630_35	630.35	0.20	0.09	-2.14	0.05	K_652_95	652.95	1.23	0.05	-4.12	0.03
K_630_78	630.78	-0.56	0.05	-1.33	0.04	K_653_25	653.25	1.29	0.04	-3.99	0.06
K_631_28	631.28	0.85	0.08	-1.34	0.04	K_653_75	653.75	1.64	0.06	-3.88	0.06
K_631_78	631.78	-0.36	0.05	-1.52	0.04	K_654_15	654.15	1.22	0.04	-3.61	0.03
K_632_23	632.23	-3.93	0.08	-1.18	0.04	K_654_65	654.65	1.47	0.07	-4.33	0.05
K_632_68	632.68	0.08	0.02	-3.15	0.03	K_655_11	655.11	1.04	0.04	-2.90	0.06
K_633_18	633.18	0.03	0.05	-2.15	0.03	K_655_61	655.61	0.82	0.06	-1.89	0.05
K_633_53	633.53	0.03	0.10	-0.82	0.08	K_656_04	656.04	0.02	0.08	-0.99	0.03
K_634_03	634.03	0.21	0.07	-0.90	0.03	K_656_54	656.54	0.23	0.10	-2.56	0.09
K_634_50	634.50	0.11	0.06	-2.58	0.01	K_656_99	656.99	0.34	0.07	-2.23	0.03
K_635_00	635.00	0.29	0.05	-1.14	0.03	K_657_49	657.49	0.78	0.08	-2.31	0.04
K_635_25	635.25	0.59	0.06	-1.76	0.05	K_657_97	657.97	0.81	0.04	-2.07	0.02
K_635_80	635.80	0.70	0.07	-0.84	0.04	K_658_47	658.47	0.86	0.06	-3.03	0.04
K_636_15	636.15	0.73	0.05	-0.83	0.02	K_658_97	658.97				
K_636_75	636.75	1.26	0.02	-2.47	0.05	K_659_42	659.42	1.58	0.05	-2.92	0.08
K_637_08	637.08	1.63	0.07	-0.72	0.07	K_659_89	659.89	1.63	0.08	-3.00	0.03
K_637_53	637.53	1.26	0.06	-2.86	0.04	K_660_39	660.39	1.70	0.05	-3.49	0.05
K_637_98	637.98	0.45	0.07	-2.27	0.05	K_660_71	660.71	1.23	0.07	-3.51	0.03
K_638_48	638.48	1.31	0.12	-1.96	0.06	K_661_31	661.31	1.77	0.06	-3.81	0.04
K_638_91	638.91	0.46	0.02	-1.79	0.05	K_661_61	661.61	1.73	0.03	-3.67	0.04
K_639_41	639.41	1.37	0.11	-1.20	0.05	K_662_05	662.05	1.68	0.05	-2.61	0.03
K_639_82	639.82	1.68	0.05	-1.60	0.02	K_662_75	662.75	1.68	0.03	-3.13	0.04
K_640_32	640.32	2.30	0.11	-1.18	0.04	K_663_13	663.13	1.84	0.08	-1.15	0.04
K_640_78	640.78	2.22	0.06	-1.06	0.04	K_663_63	663.63	1.80	0.06	-2.45	0.04
K_641_33	641.33	1.65	0.10	-1.05	0.04	K_664_04	664.04	1.87	0.08	-2.57	0.08
K_641_73	641.73	0.76	0.06	-1.67	0.03	K_664_49	664.49	1.66	0.10	-3.14	0.06
K_642_23	642.23	1.30	0.06	-0.59	0.07	K_664_93	664.93	2.14	0.05	-0.66	0.06
K_642_68	642.68	1.74	0.02	-0.17	0.03	K_665_43	665.43	2.12	0.10	-0.36	0.07
K_643_22	643.22	1.31	0.05	-3.72	0.03	K_665_88	665.88	1.49	0.05	-2.12	0.03
K_643_49	643.49	0.98	0.03	-3.57	0.07	K_666_38	666.38	1.65	0.04	-2.70	0.03
K_643_94	643.94	1.07	0.07	-3.85	0.04	K_666_74	666.74	1.30	0.05	-3.13	0.05
K_644_25	644.25	1.21	0.07	-3.60	0.06	K_667_19	667.19	1.41	0.07	-4.21	0.04
K_644_75	644.75	0.99	0.03	-3.48	0.04	K_667_54	667.54	1.68	0.06	-4.19	0.07
K_645_15	645.15	1.42	0.04	-3.48	0.04	K_668_04	668.04	1.77	0.09	-4.01	0.05
K_645_65	645.65	1.41	0.06	-3.14	0.05	K_668_37	668.37	1.16	0.05	-3.42	0.03
K_645_98	645.98	1.65	0.13	-2.43	0.06	K_668_87	668.87	1.35	0.08	-3.61	0.04
K_646_48	646.48	1.85	0.07	-2.98	0.07	K_669_27	669.27	0.68	0.08	-3.80	0.03

Sample	Depth (m)	δ¹³C VPDB	s.d.	δ¹⁸O VPDB	s.d.	Sample	Depth (m)	δ¹³C VPDB	s.d.	δ¹⁸O VPDB	s.d.
K_669_53	669.53	1.05	0.03	-3.22	0.02	K_692_45	692.45	1.68	0.05	-2.12	0.04
K_670_08	670.08	1.11	0.05	-3.26	0.03	K_692_95	692.95	2.10	0.05	-2.76	0.03
K_670_55	670.55	1.95	0.07	-2.47	0.02	K_693_48	693.48	2.70	0.06	-2.15	0.04
K_671_05	671.05	2.07	0.07	-3.66	0.04	K_693_88	693.88	2.52	0.08	-2.28	0.03
K_671_54	671.54	1.15	0.09	-2.06	0.04	K_694_36	694.36	2.19	0.06	-2.36	0.05
K_672_04	672.04	1.11	0.07	-2.42	0.05	K_694_86	694.86	2.30	0.06	-2.35	0.05
K_672_45	672.45	1.29	0.06	-4.25	0.04	K_695_35	695.35	2.66	0.09	-3.22	0.03
K_672_95	672.95	1.04	0.06	-3.87	0.06	K_695_80	695.80	1.58	0.11	-3.20	0.08
K_673_35	673.35	1.31	0.05	-3.89	0.03	K_696_27	696.27	1.92	0.05	-2.87	0.03
K_673_85	673.85	1.47	0.06	-3.67	0.04	K_696_77	696.77	2.30	0.08	-2.68	0.10
K_674_35	674.35	1.84	0.09	-3.37	0.11	K_697_10	697.10	1.93	0.06	-2.49	0.06
K_674_70	674.70	1.38	0.04	-2.67	0.05	K_697_60	697.60	2.01	0.04	-2.70	0.04
K_675_24	675.24	1.35	0.08	-3.01	0.07	K_698_10	698.10	2.23	0.07	-2.74	0.06
K_675_69	675.69	1.74	0.08	-4.31	0.06	K_698_41	698.41	2.17	0.08	-2.74	0.05
K_676_19	676.19	1.65	0.06	-3.74	0.02	K_698_91	698.91	1.66	0.09	-3.68	0.07
K_676_79	676.79	1.58	0.06	-3.02	0.03	K_699_22	699.22	1.58	0.05	-2.99	0.04
K_677_24	677.24	1.88	0.02	-3.23	0.04	K_699_77	699.77	1.45	0.09	-3.10	0.05
K_677_59	677.59	1.80	0.04	-3.46	0.05	K_700_16	700.16	1.21	0.07	-2.65	0.06
K_677_77	677.77	1.78	0.06	-3.00	0.14	K_700_61	700.61	0.85	0.06	-3.61	0.02
K_678_32	678.32	1.98	0.06	-3.13	0.04	K_701_06	701.06	-0.07	0.07	-2.11	0.05
K_679_03	679.03	1.84	0.02	-3.46	0.03	K_701_56	701.56	-0.06	0.02	-2.91	0.05
K_679_38	679.38	1.66	0.08	-3.48	0.04	K_702_02	702.02	0.58	0.07	-2.98	0.05
K_679_75	679.75	1.84	0.07	-2.93	0.05	K_702_52	702.52	1.03	0.07	-2.99	0.04
K_680_25	680.25	2.14	0.11	-3.32	0.07	K_702_92	702.92	0.51	0.05	-3.86	0.02
K_680_65	680.65	1.82	0.07	-2.31	0.05	K_703_42	703.42				
K_681_15	681.15	2.10	0.09	-3.34	0.06	K_703_83	703.83	-2.88	0.10	-0.31	0.07
K_681_55	681.55	1.89	0.08	-3.09	0.04	K_704_28	704.28	-2.30	0.01	-1.09	0.04
K_682_05	682.05	1.16	0.06	-2.98	0.04	K_704_73	704.73	-0.30	0.04	-4.42	0.02
K_682_49	682.49	1.57	0.04	-3.40	0.07	K_705_23	705.23	-1.72	0.06	-3.28	0.07
K_682_99	682.99	1.80	0.10	-3.65	0.08	K_705_67	705.67	-0.02	0.02	-4.58	0.03
K_683_43	683.43	1.73	0.05	-3.73	0.01	K_706_12	706.12	-1.61	0.07	-4.04	0.06
K_683_93	683.93	1.94	0.07	-3.27	0.04	K_706_35	706.35	-0.46	0.02	-5.17	0.05
K_684_37	684.37	1.91	0.08	-3.63	0.05	K_706_65	706.65	-0.12	0.08	-4.85	0.06
K_684_87	684.87	1.46	0.10	-3.45	0.05	K_707_15	707.15	-1.66	0.05	-2.43	0.03
K_685_28	685.28	1.69	0.04	-3.58	0.03	K_707_55	707.55	-0.30	0.03	-4.92	0.06
K_685_78	685.78	1.37	0.06	-3.55	0.04	K_708_05	708.05	-0.39	0.08	-4.62	0.05
K_686_25	686.25	1.68	0.06	-3.25	0.06	K_708_50	708.50	-0.86	0.07	-3.93	0.04
K_686_75	686.75	1.37	0.09	-3.32	0.03	K_709_05	709.05	-0.62	0.04	-4.81	0.02
K_687_10	687.10	0.92	0.10	-2.80	0.04	K_709_42	709.42	-0.39	0.04	-5.23	0.04
K_687_60	687.60	1.19	0.06	-3.21	0.05	K_709_92	709.92	0.05	0.07	-4.30	0.04
K_687_93	687.93	1.58	0.04	-4.02	0.05	K_710_30	710.30	-0.28	0.06	-5.01	0.03
K_688_43	688.43	1.22	0.06	-4.39	0.06	K_710_85	710.85	0.56	0.08	-4.18	0.03
K_688_75	688.75	1.50	0.09	-3.75	0.06	K_711_38	711.38	0.74	0.09	-3.76	0.06
K_689_25	689.25	1.39	0.04	-3.41	0.05	K_711_88	711.88	-0.22	0.07	-4.61	0.04
K_689_63	689.63	1.61	0.03	-3.05	0.02	K_712_33	712.33	0.16	0.04	-4.41	0.03
K_690_18	690.18	1.46	0.05	-3.21	0.03	K_712_78	712.78	0.64	0.06	-4.55	0.03
K_690_45	690.45	1.44	0.07	-2.77	0.03	K_713_24	713.24	0.74	0.07	-4.36	0.02
K_691_20	691.20	2.04	0.02	-2.83	0.03	K_713_74	713.74	0.67	0.07	-4.75	0.06
K_691_56	691.56	2.21	0.07	-2.42	0.04	K_714_16	714.16	1.14	0.03	-4.21	0.04
K_692_11	692.11	0.57	0.07	-2.12	0.05	K_714_56	714.56	0.95	0.05	-4.53	0.05

Appendix

Sample	Depth (m)	δ¹³C VPDB	s.d.	δ¹⁸O VPDB	s.d.	Sample	Depth (m)	δ¹³C VPDB	s.d.	δ¹⁸O VPDB	s.d.
K_714_86	714.86	0.91	0.08	-3.81	0.03	K_737_78	737.78	2.96	0.07	-1.45	0.06
K_715_16	715.16	1.17	0.04	-4.11	0.05	K_738_25	738.25	2.46	0.06	-1.45	0.04
K_715_60	715.60	0.26	0.05	-3.43	0.02	K_738_75	738.75	3.25	0.07	-1.99	0.04
K_716_10	716.10	0.39	0.06	-3.06	0.07	K_739_18	739.18	3.04	0.08	-2.55	0.06
K_716_69	716.69	1.20	0.11	-4.20	0.08	K_739_68	739.68	2.56	0.06	-2.27	0.06
K_717_14	717.14	1.16	0.09	-4.16	0.07	K_740_15	740.15				
K_717_49	717.49	1.06	0.05	-3.97	0.03	K_740_65	740.65	2.09	0.08	-1.96	0.06
K_717_99	717.99	0.77	0.02	-3.57	0.07	K_741_05	741.05	2.36	0.09	-3.20	0.04
K_718_39	718.39	1.14	0.08	-3.78	0.04	K_741_28	741.28	2.60	0.06	-2.58	0.04
K_718_94	718.94	1.17	0.07	-3.33	0.03	K_741_83	741.83	3.81	0.08	-0.90	0.06
K_719_30	719.30	1.11	0.11	-3.38	0.06	K_742_25	742.25	2.80	0.08	-2.08	0.07
K_719_80	719.80	0.50	0.06	-4.37	0.03	K_742_70	742.70	2.34	0.09	-2.78	0.04
K_720_25	720.25	0.60	0.07	-3.56	0.07	K_743_12	743.12	2.98	0.09	-2.67	0.05
K_720_75	720.75	0.91	0.06	-3.72	0.04	K_743_62	743.62	2.42	0.11	-2.65	0.06
K_721_16	721.16	0.74	0.11	-3.83	0.05	K_744_08	744.08	3.17	0.12	-2.32	0.12
K_721_63	721.63	-1.07	0.02	-1.76	0.04	K_744_58	744.58	2.25	0.11	-2.50	0.05
K_722_04	722.04	-0.23	0.08	-3.26	0.07	K_745_03	745.03	2.73	0.04	-2.28	0.03
K_722_54	722.54	0.62	0.09	-3.47	0.03	K_745_53	745.53	2.93	0.09	-2.25	0.05
K_722_99	722.99	0.89	0.06	-3.72	0.05	K_746_03	746.03	3.12	0.06	-2.17	0.07
K_723_49	723.49	0.84	0.08	-2.70	0.04	K_746_48	746.48	2.49	0.09	-2.30	0.06
K_723_94	723.94	-1.72	0.10	-1.52	0.06	K_746_87	746.87	2.04	0.11	-1.82	0.08
K_724_39	724.39	0.62	0.10	-3.83	0.07	K_747_35	747.35	0.51	0.06	-1.95	0.04
K_724_79	724.79	-0.37	0.03	-2.81	0.06	K_747_72	747.72	1.01	0.08	-1.67	0.04
K_725_29	725.29	0.21	0.05	-3.92	0.03	K_748_27	748.27	0.60	0.05	-3.69	0.05
K_725_63	725.63	-0.76	0.04	-3.43	0.02	K_748_64	748.64	-0.34	0.11	-0.79	0.06
K_726_18	726.18	-1.29	0.06	-3.13	0.05	K_749_14	749.14	-0.21	0.07	-3.04	0.04
K_726_46	726.46	-1.82	0.05	-3.14	0.03	K_749_53	749.53	1.63	0.04	-3.51	0.02
K_726_96	726.96	-1.31	0.10	-2.39	0.03	K_749_93	749.93	3.92	0.07	-1.62	0.06
K_727_40	727.40					K_750_25	750.25	2.64	0.05	-2.65	0.06
K_727_85	727.85	-2.14	0.08	-1.97	0.06	K_750_75	750.75	2.63	0.04	-2.49	0.03
K_728_33	728.33	-0.41	0.07	-2.96	0.05	K_751_18	751.18	1.64	0.04	-2.15	0.04
K_728_83	728.83					K_751_68	751.68	2.60	0.07	-2.04	0.07
K_729_18	729.18	-0.49	0.08	-3.27	0.04	K_752_15	752.15	0.48	0.05	-1.96	0.03
K_729_68	729.68	-1.80	0.08	-3.35	0.08	K_752_65	752.65	1.54	0.04	-2.95	0.05
K_730_10	730.10	0.27	0.10	-2.24	0.07	K_753_14	753.14	2.62	0.07	-2.25	0.04
K_730_60	730.60	-9.86	0.04	2.20	0.05	K_753_64	753.64	2.69	0.07	-2.04	0.05
K_730_88	730.88	-8.76	0.07	-1.43	0.04	K_754_07	754.07	3.32	0.05	-2.27	0.07
K_731_33	731.33					K_754_62	754.62	-0.84	0.09	-3.25	0.05
K_731_73	731.73	1.27	0.08	-3.43	0.03	K_755_08	755.08	2.40	0.13	-2.30	0.07
K_732_13	732.13	-4.16	0.06	-3.22	0.06	K_755_53	755.53	3.18	0.04	-2.73	0.04
K_732_81	732.81	2.71	0.08	-2.03	0.07	K_755_95	755.95	3.06	0.08	-2.31	0.07
K_733_66	733.66	-1.05	0.03	-3.98	0.03	K_756_40	756.40	3.16	0.07	-2.34	0.02
K_734_16	734.16	1.05	0.08	-4.54	0.08	K_756_85	756.85	3.13	0.10	-2.63	0.07
K_734_60	734.60	3.04	0.08	-2.18	0.03	K_757_35	757.35	0.94	0.10	-3.98	0.05
K_735_10	735.10	3.33	0.07	-2.41	0.06	K_757_73	757.73	1.99	0.10	-1.95	0.03
K_735_55	735.55	3.48	0.11	-2.12	0.05	K_758_18	758.18	1.11	0.08	-3.78	0.07
K_736_05	736.05	2.72	0.04	-2.15	0.05	K_758_79	758.79	0.65	0.11	-3.46	0.10
K_736_48	736.48	2.71	0.06	-1.00	0.04	K_759_34	759.34	2.85	0.12	-2.14	0.09
K_736_98	736.98	2.69	0.06	-2.63	0.05	K_759_70	759.70	2.74	0.07	-2.08	0.07
K_737_28	737.28	2.96	0.07	-1.45	0.06	K_760_20	760.20	2.28	0.07	-2.38	0.06

Sample	Depth (m)	δ¹³C VPDB	s.d.	δ¹⁸O VPDB	s.d.	Sample	Depth (m)	δ¹³C VPDB	s.d.	δ¹⁸O VPDB	s.d.
K_760_56	760.56	1.66	0.10	-1.94	0.03						
K_761_06	761.06	-1.57	0.08	-2.25	0.06						
K_761_41	761.41	1.00	0.05	-1.34	0.02						
K_761_86	761.86	0.11	0.06	-3.26	0.04						
K_762_31	762.31	1.16	0.09	-2.92	0.07						
K_762_81	762.81	-0.74	0.05	-2.81	0.04						
K_763_15	763.15	-0.54	0.05	-3.31	0.05						
K_763_65	763.65	1.33	0.07	-2.49	0.05						
K_764_07	764.07	-1.43	0.10	-0.52	0.05						
K_764_57	764.57	0.35	0.02	-4.32	0.07						
K_764_97	764.97	2.68	0.08	-2.31	0.05						
K_765_47	765.47	2.86	0.10	-2.18	0.03						
K_766_00	766.00	1.75	0.05	-2.60	0.04						
K_766_40	766.40	1.54	0.04	-2.06	0.03						
K_766_79	766.79	-2.19	0.05	-2.51	0.03						
K_767_34	767.34	0.36	0.12	-2.84	0.06						
K_767_80	767.80	0.88	0.07	-3.37	0.02						
K_768_20	768.20	1.83	0.10	-1.56	0.07						
K_768_66	768.66	-1.87	0.03	-3.43	0.05						
K_769_16	769.16	0.44	0.09	-2.15	0.05						
K_769_53	769.53	-0.33	0.04	-3.73	0.03						
K_769_98	769.98	-1.48	0.07	-3.74	0.05						
K_770_38	770.38	-1.85	0.05	-3.74	0.03						
K_770_88	770.88	-0.22	0.02	-3.35	0.03						
K_771_31	771.31	-1.47	0.06	-4.36	0.03						
K_771_76	771.76	-1.22	0.05	-4.01	0.03						
K_772_24	772.24	-2.15	0.02	-5.04	0.06						
K_772_74	772.74	-0.65	0.07	-4.85	0.05						
K_773_12	773.12										
K_774_25	774.25	1.62	0.07	-1.08	0.06						
K_774_75	774.75	-2.03	0.05	-1.03	0.05						
K_775_08	775.08	-4.26	0.02	-2.44	0.04						
K_775_48	775.48	-1.64	0.07	-2.20	0.02						
K_776_08	776.08	-14.73	0.06	-3.33	0.09						
K_776_48	776.48	-1.46	0.03	-1.84	0.02						
K_776_89	776.89	-0.74	0.06	-1.47	0.05						
K_777_39	777.39	0.68	0.10	-1.06	0.05						
K_777_92	777.92	0.22	0.07	-1.74	0.03						
K_778_32	778.32	-0.52	0.05	-2.04	0.05						

Appendix

Appendix 11 Carbon and oxygen isotope results of drilled powder, Osterwald section

Sample	Depth (m)	δ13C VPDB	s.d.	δ18O VPDB	s.d.	Sample	Depth (m)	δ13C VPDB	s.d.	δ18O VPDB	s.d.
OSW 01	0	1.93	0.14	-3.60	0.10	OSW 47	25	1.83	0.15	-3.15	0.11
OSW 02	0.5	1.51	0.07	-4.19	0.04	OSW 48	25.5	0.45	0.21	-3.89	0.09
OSW 03	1	1.55	0.15	-4.36	0.07	OSW 49	26	-0.07	0.12	-4.15	0.11
OSW 04	1.5	1.88	0.13	-3.77	0.10						
OSW 05	2	2.22	0.21	-2.95	0.11						
OSW 06	2.5	1.70	0.10	-3.96	0.10						
OSW 07	3	1.83	0.18	-4.00	0.10						
OSW 08	3.5	1.83	0.17	-3.93	0.09						
OSW 09	4	1.79	0.17	-4.20	0.11						
OSW 10	4.5	1.78	0.09	-4.04	0.10						
OSW 11	5	2.07	0.13	-2.66	0.12						
OSW 12	5.5	1.53	0.13	-3.72	0.11						
OSW 13	6	2.19	0.20	-3.09	0.10						
OSW 14	6.5	2.26	0.22	-3.05	0.11						
OSW 15	7	2.18	0.21	-3.07	0.09						
OSW 16	7.5	1.40	0.11	-4.15	0.07						
OSW 17	8	2.30	0.12	-3.14	0.10						
OSW 17	8.5	2.08	0.07	-2.99	0.15						
OSW 18	9	2.11	0.20	-3.73	0.12						
OSW 19	9.5	1.90	0.11	-3.56	0.09						
OSW 19	10	1.80	0.07	-3.35	0.08						
OSW 20	10.5	2.01	0.17	-3.61	0.12						
OSW 21	11	1.97	0.20	-4.16	0.10						
OSW 22	11.5	1.97	0.18	-4.05	0.10						
OSW 23	12	2.18	0.16	-3.65	0.09						
OSW 24	12.5	2.45	0.23	-3.34	0.04						
OSW 24	13	2.16	0.05	-3.36	0.07						
OSW 25	13.5	1.95	0.12	-3.97	0.12						
OSW 26	14	1.98	0.16	-4.03	0.13						
OSW 27	14.5	2.49	0.22	-3.61	0.08						
OSW 28	15	1.95	0.07	-3.88	0.12						
OSW 29	15.5	2.17	0.14	-3.59	0.11						
OSW 30	16	2.34	0.13	-3.92	0.10						
OSW 31	16.5	1.88	0.17	-3.94	0.10						
OSW 32	17	1.85	0.13	-4.06	0.12						
OSW 33	17.5	2.25	0.21	-3.59	0.09						
OSW 34	18	2.13	0.07	-3.68	0.10						
OSW 35	18.5	2.32	0.12	-3.74	0.12						
OSW 36	19	1.43	0.16	-4.20	0.11						
OSW 37	19.5	1.27	0.05	-4.12	0.11						
OSW 38	20	1.99	0.19	-3.90	0.09						
OSW 39	20.5	1.68	0.09	-3.86	0.10						
OSW 40	21	2.21	0.23	-3.75	0.06						
OSW 41	21.5	1.38	0.13	-3.89	0.10						
OSW 42	22	1.22	0.12	-3.99	0.13						
OSW 43	22.5	0.66	0.08	-4.06	0.10						
OSW 44	23	0.64	0.09	-4.06	0.11						
OSW 45	23.5	-0.04	0.08	-4.16	0.09						
OSW 46	24	0.42	0.11	-3.73	0.08						
OSW 47	24.5	1.33	0.22	-3.21	0.05						

Appendix 12 Carbon and oxygen isotope results of drilled powder, Osterwald section

Sample	Depth (m)	δ13C VPDB	s.d.	δ18O VPDB	s.d.		
2PT-1	0.1	1.18	0.15	-2.77	0.14		
2PT-1	0.1	1.12	0.18	-2.94	0.12		
2PT-2	0.55	0.60	0.14	-1.57	0.11		
2PT-3	1.1	0.62	0.13	-1.98	0.10		
2PT-4	1.9	1.27	0.11	-2.81	0.10		
1PT-21(2PT-4)	1.9	0.28	0.12	-3.09	0.14		
PT2-5	2.6	0.56	0.06	-1.45	0.13		
2PT-5	2.6	1.50	0.19	-1.61	0.13		
1PT-19(2PT-5)	2.6	0.59	0.07	-1.84	0.15		
PT2-6	3	0.82	0.09	-0.94	0.14		
PT2-7	3.7	1.15	0.16	-0.88	0.12		
PT2-8	4.2	0.30	0.12	-1.91	0.13		
PT2-9	4.45	0.41	0.13	-1.33	0.11		
PT2-10	4.75	0.82	0.13	-1.23	0.14		
PT2-10	4.75	0.87	0.11	-1.11	0.15		
PT2-11	5.52	0.37	0.12	-0.47	0.12		
PT2-12	5.55	0.46	0.14	-1.21	0.10		
PT2-12	6.05	0.80	0.11	-1.82	0.11		
OSW-11		1.85	0.13	-4.06	0.10		
OSW-13		1.37	0.14	-4.82	0.10		

Appendix

Appendix 13 Carbon and oxygen isotope results of drilled powder, Langenberg section

Sample	Depth (m)	δ¹³C VPDB	s.d.	δ¹⁸O VPDB	s.d.	Sample	Depth (m)	δ¹³C VPDB	s.d.	δ¹⁸O VPDB	s.d.
LJ1	0	2.44	0.08	-2.29	0.10						
LJ2	0.25	2.44	0.08	-1.90	0.11						
LJ3	0.5	2.43	0.09	-1.37	0.09						
LJ4	0.75	2.36	0.10	-1.22	0.10						
LJ5	1	2.34	0.09	-0.96	0.09						
LJ6	1.25	2.18	0.08	-1.06	0.08						
LJ7	1.5	2.07	0.10	-0.78	0.11						
LJ8	1.75	1.90	0.08	-1.03	0.10						
LJ9	2	2.20	0.09	0.19	0.08						
LJ10	2.25	2.03	0.10	0.43	0.10						
LJ11	2.5	1.99	0.08	0.44	0.12						
LJ12	2.75	1.43	0.09	-1.00	0.09						
LJD1	3	2.14	0.07	-0.23	0.08						
LJD2	3.5	2.24	0.10	-0.95	0.08						
LJD3	4	2.26	0.09	-1.38	0.09						
LJD4	4.5	2.48	0.08	-1.50	0.07						
LJD5	5	2.53	0.08	0.10	0.09						
LJD6	5.5	2.63	0.07	0.47	0.05						
LJD7	6	2.71	0.09	0.71	0.10						
LJD8	6.5	2.21	0.06	-0.46	0.06						
LJD9	7	2.20	0.10	-1.36	0.09						
LJD10	7.5	2.62	0.09	-0.38	0.08						
LJD11	8	2.44	0.09	-2.50	0.08						
LJD12	8.5	2.41	0.08	-3.92	0.05						
LJD13	9	2.26	0.08	-3.88	0.07						
LJD14	9.5	2.36	0.06	-2.38	0.07						
LJD15	10	2.53	0.05	-0.07	0.09						
LJD16	10.5	2.35	0.06	-1.82	0.10						
LJD17	11	2.62	0.09	-1.34	0.08						
LJD18	11.5	2.68	0.09	-3.64	0.07						
LJD19	12	2.76	0.10	-2.50	0.09						
LJD20	12.5	2.58	0.05	-3.17	0.09						
LJD21	13	2.58	0.04	-3.44	0.08						
LJD22	13.5	2.50	0.06	-3.25	0.05						
LJD23	14	2.68	0.09	-3.33	0.11						
LJD24	14.5	2.99	0.07	-1.38	0.07						
LJD25	15	2.60	0.09	-3.66	0.07						
LJD26	15.5	2.99	0.04	-2.95	0.08						
LJD27	16	2.78	0.05	-2.89	0.07						

Appendix 14 Trace element data, Bisperode and Konrad core

Sample	Depth (m)	Ca		Mg		Sr		Fe		Mn		Unit
		$\overline{X}$	±S	$\overline{X}$	±S	$\overline{X}$	±S	$\overline{X}$	±S	$\overline{X}$	±S	
SB7.7	44	387760	4169	2634	10	592	2.5	68	0.6	16	0.3	ppm
SB8.5-A	45	370700	4347	5327	19	159	1.7	456	1.8	99	0.5	ppm
SB8.5-B	45	390570	3012	1756	6	566	2.1	218	1.8	19	0.1	ppm
SB8.5-C	45	386250	3273	3830	19	103	2.3	275	1.4	46	0.3	ppm
SB8.5-D	45	381560	2036	1623	11	542	4.9	94	0.8	12	0.0	ppm
DY10	10	386790	1984	1364	6	537	3.3	293	0.6	23	0.1	ppm
DY11.5	12.15	395480	4039	743	4	621	1.7	334	1.6	13	0.1	ppm
SB25.2	61.5	362740	2160	3813	13	645	1.5	201	0.6	32	0.1	ppm
SB57.2	94	388150	2727	1436	11	617	4.4	112	1.1	7	0.1	ppm
SB58.5	95	385200	4927	3578	6	420	2.1	1285	2.2	73	0.1	ppm
SB60.5-A	97	393070	1426	2044	11	466	2.2	194	0.9	21	0.1	ppm
SB60.5-B	97	397700	3484	1079	6	618	2.6	90	1.1	9	0.2	ppm
SB65-A	101.5	395520	2659	4010	12	289	3.2	109	1.8	57	0.3	ppm
SB65-B	101.5	391500	2998	3763	17	189	2.5	269	15.1	76	0.5	ppm
SB65-C	101.5	372420	1671	3473	20	185	1.4	316	2.1	69	0.6	ppm
D82.5-A	119	390990	2985	6171	28	622	2.2	3885	20.8	70	0.2	ppm
D82.5-B	119	386050	3438	5093	27	666	4.5	252	1.4	29	0.2	ppm
LPb-3	24.5	389840	3739	1778	10	450	2.8	686	4.1	31	0.3	ppm
LPb-6.5A	28	388210	4496	796	5	562	2.3	552	2.2	62	0.2	ppm
LPb-6.5B	28	385990	5816	2125	10	571	2.6	216	1.5	23	0.1	ppm
LPb-8.5	30	395050	2215	704	7	530	3.9	319	2.5	34	0.1	ppm
LPb-8.5B	30	390350	3336	1189	6	600	3.8	275	1.2	29	0.1	ppm
LPb-8.5D	30	361870	2938	5658	18	48	1.0	1477	6.2	95	0.7	ppm
K649.5A	649.5	384440	3839	1845	5	666	3.7	2073	6.2	99	0.4	ppm
K649.5B	649.5	360690	4180	3181	16	775	2.9	5592	17.8	136	0.4	ppm
K655.79A	655.79	315340	1686	3089	18	248	2.7	2102	123.	316	1.7	ppm
K655.79B	655.79	359550	1122	2638	14	440	1.9	11660	68.4	235	1.1	ppm
K748.2	748.2	369010	2540	1288	7	914	3.0	4078	17.3	380	1.4	ppm
K753.5	753.5	373700	5010	697	7	584	4.3	3240	12.6	259	1.3	ppm
K776.48	776.48	346380	3110	234	2	480	3.7	221	0.7	50	0.3	ppm
K776.7	776.7	394910	4134	380	3	503	3.3	1380	4.0	59	0.1	ppm
K777.45	777.45	376450	3575	3643	14	567	5.1	10110	38.6	142	0.7	ppm
K777.7	777.7	372010	3855	423	7	485	3.5	559	1.3	66	0.2	ppm
K778.40A	778.40	394080	1943	637	8	518	1.1	677	2.6	76	0.4	ppm
K778.40B	778.40	388340	3822	502	8	496	3.1	4994	15.6	77	0.3	ppm

Appendix

Appendix 15 Strontium isotope values

Section	Sample	Depth (m)	$^{87}Sr/^{86}Sr$ measured	± 2 s mean	$^{87}Sr/^{86}Sr$ sample corrected to difference: NBS 987 value McArthur and NBS 987 measured with sample	$^{87}Sr/^{86}Sr$ sample corrected to difference: USGS EN-1 value McArthur and USGS EN-1 measured with sample	$^{87}Sr/^{86}Sr$ sample corrected to difference: NBS 987 value McArthur and NBS 987 Bochum mean value	$^{87}Sr/^{86}Sr$ sample corrected to difference: USGS EN-1 value McArthur and USGS EN-1 Bochum mean value
Bisperode	DY11.5	11.5	0.706873	0.000005	0.706857	0.706869	0.706878	0.706887
	LPb-8.5B	30	0.706900	0.000005	0.706884	0.706896	0.706905	0.706914
	SB8.5-B	45	0.706898	0.000005	0.706899	0.706906	0.706903	0.706913
	SB7.7	44.2	0.706939	0.000005	0.706923	0.706935	0.706944	0.706954
	SB25.2	61.7	0.706894	0.000005	0.706878	0.706890	0.706899	0.706909
	SB60.5-B	97	0.706909	0.000005	0.706893	0.706905	0.706914	0.706923
	D82.5-B	119	0.706900	0.000005	0.706884	0.706896	0.706905	0.706914
Konrad core	K748.2	748.2	0.706935	0.000005	0.706919	0.706931	0.706940	0.706950
	K753.5	753.5	0.706951	0.000005	0.706952	0.706959	0.706956	0.706966
	K649.5A	649.5	0.706967	0.000005	0.706951	0.706963	0.706972	0.706981
	K649.5B	649.5	0.707178	0.000007	0.707162	0.707174	0.707183	0.707193

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