Micropaleontology and Isotope Stratigraphy of the Upper Aptian to Lower Cenomanian (~114-98 Ma) In ODP Site 763, Exmouth Plateau, NW Australia

Ali Alibrahim

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MICROPALEONTOLOGY AND ISOTOPE STRATIGRAPHY OF THE UPPER APTIAN TO LOWER CENOMANIAN (~114-98 MA) IN ODP SITE 763, EXMOUTH PLATEAU, NW AUSTRALIA

A Thesis Presented

by

ALI H. ALIBRAHIM

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of MASTERS OF SCIENCE

May 2016

GEOSCIENCES
MICROPALEONTOLOGY AND ISOTOPE STRATIGRAPHY OF THE UPPER APTIAN TO LOWER CENOMANIAN (~114-98 MA) IN ODP SITE 763, EXMOUTH PLATEAU, NW AUSTRALIA

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Approved as to style and content by:

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R. Mark Leckie, Chair

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Steven Petsch, Member

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Robert M. DeConto, Member

_________________________________________________
Steven Petsch
Graduate Program Director, Geosciences Department
DEDICATION

For my wife and daughter, for filling my life with love and happiness.
For my mother and father who raised me up, taught me through my early years and encouraged me to learn everyday.
ACKNOWLEDGEMENTS

I thank Professor Mark Leckie for his kind leadership and guidance and for all the educational discussions and seminars he conducted. I also thank every member of the micropaleontology lab for helping me through all the challenges, Andy Fraass, Renata DeMello, Serena Dameron, Amanda Parker, Chris Lowery and Khalifa Elderbak. I appreciate the support of my committee members Professors Steven Petsch and Rob DeConto. My research benefited greatly from the Bio-geochemistry class of Professor Steven Petsch and the isotope geochemistry class of Professor Stephen Burns.

I thank Dr. Geraint Wyn ap Gwylim Hughes for introducing me to the field of micropaleontology in Saudi Aramco.

I thank the people at Saudi Aramco who approved my scholarship and trusted me to successfully conduct long term research in micropaleontology.
ABSTRACT

MICROPALEONTOLOGY AND ISOTOPE STRATIGRAPHY OF THE UPPER APTIAN TO LOWER CENOMANIAN (~114-98 MA) IN ODP SITE 763, EXMOUTH PLATEAU, NW AUSTRALIA

MAY, 2016

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Directed by: Professor R. Mark Leckie

The biostratigraphy and isotope stratigraphy of the upper Aptian to lower Cenomanian interval including oceanic anoxic events OAE1b, 1c and 1d are investigated in ODP Site 763, drilled on the Exmouth Plateau offshore northwest Australia. Benthic foraminifera suggest that Site 763 was situated in outer neritic to upper bathyal water depths (~150-600 m). OAEs of the Atlantic basin and Tethys are typically associated with organic carbon-rich black shales and $\delta^{13}$C excursions. However, OAEs at this high latitude site correlate with ocean acidification and/or pyrite formation under anoxic conditions rather than black shales. Ocean acidification maybe responsible for sporadic low abundances of planktic foraminifera compared to radiolarians and benthic foraminifera associated with increased volcanogenic CO$_2$ production during the formation of the Southern and Central Kerguelen Plateaus. Sea surface temperature may have cooled to 11°C in the late Aptian but increased gradually during the Albian. The Aptian/Albian boundary is placed at a negative carbon isotope excursion associated with the lowest occurrence of Microhedbergella renilaevis, typically found within the Niveau Kilian black shale of OAE1b. Third-order sea level cycles, particularly in the middle Albian, produced cyclic changes in the abundance of inoceramid prisms that increased during inferred times of falling sea level. The late Albian OAE1c and OAE1d coincide with horizons of intense pyritization and the absence of all biocomponents suggesting the
development of euxinia. Warm Tethyan waters reached the Exmouth Plateau during the latest Albian based on the presence of thermocline dwelling keeled planktic foraminifera including Planomalina buxtorfi.
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CHAPTER 1
INTRODUCTION

Oceanic Anoxic Events (OAEs) are intervals of widespread burial and preservation of organic carbon under anoxic conditions typically forming black shales with ~1.0-2.5‰ excursions (positive or negative) in the $\delta^{13}C$ record of carbonates and associated organic matter (Figure 1) [e.g., Bralower et al., 1993; Leckie et al., 2002; Erba, 2004; Jenkyns, 2010; Huber and Leckie, 2011]. Schlanger and Jenkyns (1976) introduced the term “Oceanic Anoxic Events” to describe two intervals of organic rich black shale deposition around the world that clustered around the Aptian/Albian (OAE1) and the Cenomanian/Turonian (OAE2) boundaries [Arthur and Schlanger, 1979]. Arthur and others (1990) subdivided OAE1 into three sub-events deposited as discrete black shales in the early Aptian, latest Aptian and late Albian and termed them OAE1a, 1b and 1c consecutively. OAE1c was reassigned as OAE1d, and OAE1c was assigned to a black shale interval in the early late Albian [Bralower et al., 1993; Erbacher and Thurow, 1997]. This thesis focuses on OAE1b, 1c and 1d in terms of micropaleontology and stable isotope geochemistry, and their implications for sequence stratigraphy, biostratigraphy, paleoclimatology, and paleoceanography.

Oceanic Anoxic Events are often deposited as black shales in pelagic or hemipelagic facies but their genesis, isotope content, and organic matter varies due to local and regional paleoceanographic and sedimentological conditions [Alexandre et al., 2011]. Erbacher et al., 1996 divided OAEs in two categories: Productivity OAEs (P-OAEs) and Detrital OAEs (D-OAEs) (Figure 2). P-OAE black shales typically contain type II kerogen of marine origin, have positive $\delta^{13}C$ excursions in carbonates and organic matter, and are typically deposited in transgressive systems tracts. D-OAE black shales typically contain type III kerogen of terrigenous origin, have negative $\delta^{13}C$ excursions in
carbonates and organic matter, and are deposited in lowstand systems tracts (Figure 2). Both OAE1b and OAE1d are Productivity OAEs with a wider global distribution, while OAE1c is a Detrital OAE with limited distribution [Erbacher et al., 1996; Bralower et al., 1993; Leckie et al., 2002].

The temporal and spatial relationship between OAEs and mid-Cretaceous submarine volcanism was first noted by Schlanger and Jenkyns in 1976. Most mid-Cretaceous OAEs are clustered between 120-93 Ma, which coincides with higher seafloor spreading rates and magma flux during the Cretaceous Normal Superchron (120-80 Ma) [Larson, 1991a, b; Larson and Erba, 1999; Coffin et al., 2006]. Large Igneous Provinces (LIPs) had the largest impact on Cretaceous environments due to their massive basaltic eruptions that...
released greenhouse volatiles such as CO$_2$, CH$_4$ and SO$_2$ leading to global warming [Coffin et al., 2006]. In addition, higher hydrothermal activity increased the supply of micronutrients, including dissolved iron, which enhanced organic matter production and expanded the oxygen minimum zones leading to oceanic anoxia and deposition of organic rich horizons (Figure 3) [Leckie et al., 2002; Bralower, 2008]. The strontium isotope ratios ($^{87}$Sr/$^{86}$Sr) of planktic, benthic and inoceramid bivalve shells indicate higher rates of submarine volcanism coinciding with the deposition of Aptian and Cenomanian-Turonian OAEs, followed by higher rates of continental weathering during the Albian associated with rising sea level and global warming (Figure 4)[Bralower et al., 1997; Jones and Jenkyns, 2001; Leckie et al., 2002].

Figure 2. The source of organic matter in black shales is different based on sealevel. A: A transgression leaches nutrients from lowlands to seed marine organic matter production leading to anoxia. B. Terrestrial organic matter is transported and redeposited on the shelf edge during a low stand systems tract [Erbacher et al., 1996]
Figure 3. Submarine volcanism drives hydrothermal activity, which leaches metal micronutrients seeding marine organic matter production leading to bottom water anoxia. CO$_2$ is released to the atmosphere, which leads to global warming and intensification of water column stratification, which assists black shale deposition [Bralower, 2008]
Figure 4. In the Vocontian Basin, OAE1b consists of four black shales: Jacob, Kilian, Paquier and Leenhardt. The Kilian is associated with the largest of planktic turnover in the Aptian/Albian boundary interval [Leckie et al., 2002; Huber and Leckie, 2011; Petrizzo et al., 2012; Kennedy et al., 2014]
1.2 The Aptian/Albian OAE1b

The Aptian/Albian boundary interval (113.3 – 109.0 Ma) consists of four black shale horizons that collectively define OAE1b (*sensu* Leckie et al., 2002) in the Col de Pré-Guittard section in the Vocontian Basin, SE France [Bréhéret, 1994; Kennedy et al., 2000; Herrle et al., 2004; Trabuco Alexandre et al., 2011; Petrizzo et al., 2012; Coccioni et al., 2014; Kennedy et al., 2014]. The black shale horizons are deposited as follows: Niveau Jacob (uppermost Aptian), Niveau Kilian (Aptian/Albian boundary), Niveau Paquier (lowermost Albian) and Niveau Leenhardt (upper lower Albian) (Figure 5) [Petrizzo et al., 2012; Kennedy et al., 2014]. Each black shale horizon is enriched in organic matter deposited under anoxic conditions and correlates with negative excursion in the $\delta^{13}C$ record separated by brief periods of oxygenation and pelagic carbonate deposition [Moullade et al. 2011; Coccioni et al., 2014; Kennedy et al., 2014].

![Figure 5](image.png)

Niveau Kilian black shale coincides with the most significant global evolutionary turnover (extinction plus speciation) of planktic foraminifera in the Cretaceous [Leckie et al., 2002; Petrizzo et al., 2012; Huber and Leckie, 2011]. In addition, planktic foraminifera show a severe reduction in shell size, diversity and morphological complexity. The turnover of planktic foraminifera across Niveau Kilian can be correlated globally and is not limited to sites with black shale development [Petrizzo et al., 2012; Huber and Leckie, 2011]. The turnover consists of the following events: the Highest Occurrence (HO) of Paraticinella eubejaouaensis (= P. rohri), Pseudoguembelitria blakenosensis, Hedbergella infracretacea, H. aptiana, and the Lowest Occurrence (LO) of Microhedbergella miniglobularis and Mi. renilaevis (Figure 6) [Huber and Leckie, 2011; Petrizzo et al., 2012]. In addition, the AABI can also be approximated by the LO of the circular form of the nannofossil Prediscosphaera columnata and the LO of the benthic foraminifera Pleurostomella subnodosa [Moullade, 1966; Kennedy et al., 2000; Moullade 2011; Huber and Leckie, 2011; Kennedy et al., 2014].

OAE1b black shales, in general, correlate with a global sea-level rise, rising temperatures, increased stratification, and higher productivity. Stratification is well established in the convergence of values of δ¹³C and divergence of δ¹⁸O records of epifaunal and infaunal benthics versus deep and shallow dwelling planktic foraminifera in one site from the western tropical North Atlantic ([Erbacher et al., 2001; Petrizzo et al., 2012]).
1.3 Cooling in the late Aptian and warming across the Aptian/Albian boundary

The Cretaceous, in general, is typically viewed as a greenhouse world caused by increased ocean crust production, including LIP emplacement, and CO₂ outgassing leading to rising temperatures and sea level (e.g., Larson, 1991a, b). However, there is a plethora of evidence for cool interludes in the latest Aptian with warming across the
Aptian/Albian boundary interval and through the Albian (Weissert and Lini, 1991; Clarke and Jenkyns, 1999; Huber et al., 2002; Leckie et al., 2002; Price, 2003; Mutterlose et al., 2009; Friedrich et al., 2012; Petrizzo et al., 2012; McAnena et al., 2013) (Figure 7).

For example, $\delta^{18}O$ data of belemnites from shelf environments suggest paleotemperatures between 7.7° and 11.3°C for the lower Albian Gearle Siltstone outcrops in northwest Australia (paleolatitude ~55°S) and the Rio Mayer Formation in southern Argentina (paleolatitude 57°S) [Pirrie et al., 1995; Pirrie et al., 2004], while Tethyan warm water nannoconids experienced a significant decline in latest Aptian (Leckie et al., 2002) and cool water, high latitude taxa increased in abundance in the Exmouth Plateau and the Vocontian basin [Mutterlose et al., 2009].

Figure 7. Paleotemperature estimates suggest a late Aptian cooling due to the O-isotope enrichment of planktic foraminifera and convergence with benthic values. The sea surface temperature is ~17°C and is much cooler than typical tropical Cretaceous SSTs [Leckie et al., 2002]
A late Aptian cooling probably resulted from decreasing levels of CO₂ by increased organic matter burial and/or silicate weathering [Lini and Weissert 1991; Hong and Lee, 2012; Maurer et al., 2012; McAnena et al., 2013.]

1.4 The early late Albian OAE1c

OAE1c is an early late Albian (107.18 – 106.78 Ma) black shale horizon rich in detrital organic matter, but unlike OAE1b and 1d, OAE1c is not associated with a turnover in calcareous plankton or radiolaria [Bralower et al., 1993; Erbacher, 1996; Leckie et al., 2002]. OAE1c is a DOAE that coincides with a sea level fall and higher sedimentation rates in basins close to continental hinterlands (e.g., Mazagan Plateau, NW African continental margin) [Erbacher et al., 1996]. OAE1c is poorly known. The Toolebuc Formation of the Queensland Basin, Australia, is an example of a regionally developed, correlative oil shale interval [Haig, 1979; Bralower et al., 1993].

1.5 The latest Albian OAE1d

The latest Albian interval (103.3 – 99.0 Ma) consists of several black shale horizons and a positive $\delta^{13}C$ excursion that define OAE1d (Figure 1) [Wilson and Norris, 2001; Watkins et al., 2005; Petrizzo et al., 2008; Melinte-Dobrinescu, 2015]. OAE1d was first described as a radiolarian turnover event across the uppermost Albian black shale horizon in the Le Brecce section in the Umbria-Marche basin, Italy [Erbacher and Thurow, 1997]. However, OAE1d is also associated with a major phase of biotic turnover affecting planktic foraminifera including the HO of Biticinella and Ticinella and the LO of Planomalina, Praeglobotruncana and Paracostellagerina, as well as turnover in the Rotalipora [Nederbragt et al., 2001; Leckie et al., 2002; Petrizzo et al., 2008].

Unlike the Aptian/Albian boundary interval of multiple black shales of OAE1b, the
latest Albian black shales of OAE1d are not deposited synchronously and their $\delta^{13}C$ excursion peaks do not correlate with the deposition of black shales [Petrizzo et al., 2008]. The convergence of $\delta^{18}O$ values of deep and shallow dwelling planktic and benthic foraminifera at one North Atlantic site suggests the collapse of stratification and greater mixing in the upper water column and higher productivity [Wilson and Norris, 2001; Petrizzo et al., 2008].

![Figure 8. The collapse of near surface ocean stratification is illustrated in the overlap of deep and shallow dwelling planktic foraminifera across OAE1d black shales in ODP Site 1052 [Wilson and Norris, 2001]](image)

1.6 Study Site

The Exmouth Plateau is a deep-water marginal plateau that is the westernmost extent of the North Carnarvon Basin, NW Australia. ODP Site 763 was drilled in 1988 during Ocean Drilling Program Leg 122 (20°35.19'S, 112°12.52'E) under 1367 m water depth to provide sedimentological and sequence stratigraphic data for the Cretaceous section (Figure 9) [Suess et al., 1988]. Three holes, A, B and C were drilled to a total depth of 1376.6 m with 121 cores representing the interval from the middle Berriasian to upper Eocene. The interval of interest for this research was only cored in Hole 763B between Cores 25X-41X (408.5-570.0 m) and spans the upper
Aptian-lower Cenomanian. Average core recovery was 81% for Hole 763B, but dropped to an average of 26% for four consecutive cores in the upper Aptian (Cores 38X-41X) (Figure 10) [Suess et al., 1988].

The sedimentary succession in Hole 763B was divided into 7 units based on visual descriptions and smear slide sedimentological estimates. Unit 4 was assigned to the interval from (385.72-570.00 mbsf), which was subdivided into subunits 4A (385.72-532.00 mbsf: Cores 23X-37X) and 4B (532.00-570.00 mbsf: Cores 38X-41X) based on the presence of hard carbonates and poor recovery in subunit 4B. No black shales were recovered, but the Aptian/Albian and the Albian/Cenomanian boundaries were tentatively picked shipboard at 570 mbsf and 420 mbsf, respectively, based on calcareous nannofossil and planktic foraminiferal data [Suess et al., 1988].

The Aptian/Albian boundary at Hole 763B was later picked at 528 mbsf based on the LO of *Prediscosphaera columnata* [Bralower and Siesser, 1992], and supported by a planktic turnover at 530 mbsf [Huber and Leckie, 2011].

Figure 9. Bathymetric map of the Exmouth Plateau showing ODP Site 763 off the northwest coast of Australia [Suess et al., 1988]
Figure 10. Top: Images of the interval surrounding the Aptian Albian boundary showing poor recovery of the uppermost Aptian. The Aptian/Albian boundary is placed in Section 763B-37X-5. Note the poor recovery in uppermost Aptian Cores 38X-41X.

Left: A lithostratigraphy column with the cored interval of interest. Core recovery is poor from the middle of Core 37X to the bottom of 42X as illustrated in the black and white column next to core numbers [Suess et al., 1988]. The Aptian/Albian boundary is placed in Section 763B-37-5 (Huber and Leckie, 2011).
1.7 Research Questions

1. Do the assemblage and abundance data of benthic and planktic foraminifera exhibit changes or turnovers at the intervals correlative to OAE1b, 1c and 1d?

2. What paleoceanographic and sequence stratigraphic interpretations can be drawn from sedimentological, biogenic, and foraminiferal assemblages and isotope data in ODP Hole 763B?

3. Do benthic and planktic foraminiferal assemblages and isotope records suggest reworking and an unconformity across the Aptian/Albian boundary interval?

4. Is there evidence for latest Aptian cooling at ODP Site 763?
CHAPTER 2
MATERIALS AND METHODS

A total of 138 Samples from ODP Hole 763B Cores 25X-41X were analyzed in this study with a maximum sample spacing of 1.58 m and an overall average of 1.22 m producing a 160-kyr resolution in the Albian and Cenomanian intervals and 30-kyr resolution in the Aptian. 68 Samples were originally sampled and studied by Richard Cashman and R. Mark Leckie on a 63 micron sieve [Leckie et al., 2002; Huber and Leckie, 2011]. 70 new samples were requested from the International Ocean Discovery Program core repository in Kochi, Japan; each sample was labeled using standard IODP hole, core-section, interval conventions, as well as depth in meters below seafloor (mbsf).

Samples were mechanically crushed, soaked for a week in 300 ml of Sparkleen solution, agitated daily to insure disintegration of clays in a basic solution, and then washed over a 63 µm sieve. Samples were washed a second time over a 63 µm sieve, soaked in 10 ml of water, then dried for 24 hours.

2.1 The micropaleontology survey

The micropaleontology survey was conducted on all samples by further sieving the samples on a 125 µm sieve mainly to investigate the response of benthic foraminifera to possible dysoxic-anoxic conditions across OAEs in the study interval. The study also acquired detailed counts on planktic forams, radiolarians, inoceramid prisms, and pyrite nodules.

Samples were split to achieve a smaller representative quantity of the sample, which is then analyzed on a gridded picking tray. A minimum of 300 foraminifera specimens were picked and counted regardless of the associated number of other components.
such as radiolarians and inoceramid prisms, which exceeded 1000 counts in some samples.

The number of all components were scaled up by a factor of 2 to the power of the number of splits. For example, three splits provide a 1/8 fraction of the sample, so the number of specimens found in the tray are multiplied by 8 to approximate the population in the entire 10-CC sample. The total number of components provides an accurate percentage of each component per sample. The number of planktic and benthic specimens can be expressed P/B ratio, which is the percentage of planktic and benthic specimens relative to the total number of foraminifera.

2.2 The isotope survey

The isotopic composition of the interval was conducted using 203 samples focused on four different components at different resolutions, two epifaunal benthic forams, Osangularia schloenbachi and Gavelinella spp., fine fraction (<63 µm) bulk carbonates (Bulk FF), and Microhedbergella spp. Osangularia schloenbachi (epifaunal benthic foram) was analyzed in 90 samples, and Gavelinella spp. (another epifaunal benthic) was analyzed in 44 samples, for an average of 1.22 and 3 m intervals, respectively. Bulk FF were sampled every 3 m or less (68 samples), and Microhedbergella spp. at variable spacing (27 samples).

Osangularia is the most abundant epifaunal benthic genus in the study section, which makes it ideal for a detailed isotope study; however, it is absent in the Aptian interval. The long-ranging genus Gavelinella was sampled in the entire section (Aptian-Cenomanian) to provide benthic isotopic signals in the Aptian and provide a supporting benthic isotopic signal in the Albian-Cenomanian in addition to Osangularia.

Fine fraction bulk carbonates (<63 µm) were collected during the washing phase and
were run for isotopic investigation every 3 m in the Albian-Cenomanian and every 0.86 m, on average, in the Aptian. Planktic isotopes were few because they were only used to provide control on Bulk FF isotope data and their values generally agree.

All samples were run at the University of Missouri Stable Isotope Facility using a Kiel III automated carbonate device coupled a Thermo Finnigan DeltaPlus IRMS. Results were normalized by the difference between average replicate analyses of standard carbonate material NBS-19 and nominal values of -2.2‰ and +1.95‰ for $\delta^{18}O$ and $\delta^{13}C$ consecutively.

Individual forams were hand-picked until a sample’s weight ranged between 40-80 µg; specimens were then placed in glass vials and loaded in the reaction chamber. Each vial is flushed with helium to remove air before adding phosphoric acid (H$_3$PO$_4$). Three to four drops of acid are reacted with each sample at 80°C for an hour. Liberated CO$_2$ is analyzed under a helium flow connected to a Mass Spectrometer.

### 2.3 Paleotemperature Calculation

Paleotemperatures can be estimated using the equation of Bemis et al. (1998) assuming the $\delta^{18}O_{\text{seawater}}$ is -1‰ [Schackleton and Kennett, 1975; Friedrich et al., 2012; Price et al., 2012]. However, the presence of ice caps and biological fractionations associated with planktic foraminifera may cause errors in temperature estimates.

$$T^\circ C = 16.0 - 4.14(\delta_{\text{carbonate}} - \delta_{\text{seawater}}) + 0.13(\delta_{\text{carbonate}} - \delta_{\text{seawater}})^2$$

### 2.4 Age Model

An age model is essential in calculating sedimentation rates and estimating durations of unconformities. The age model for this study was established on the Lowest Occurrence events (LO) of calcareous nanofossils from ODP Hole 763B (Bralower and
Siesser, 1992). A table of the nannofossil datums is shown in Figure 21. Numerical ages of
the nannofossil events are based on the 2012 Geological Time Scale [Gradstein et al.,
2012]. Sedimentation rates are determined by

Equation 1: \( \text{Sedimentation Rate} = \frac{\Delta \text{Depth}}{\Delta \text{Age}} \) (between two nannofossil datums)

Sample age will be determined as

\[
\text{Sample age} = \left[ \frac{1}{\text{sed rate}} \cdot (\text{Sample depth} - \text{Datum depth}) \right] + \text{Younger Datum Age}
\]

Figure 11 Nannofossil events from three ODP sites from Exmouth Plateau including ODP 763B. These events were
used to construct the age model for the studied interval (400 – 560 mbsf) [from Bralower and Siesser, 1992].
CHAPTER 3
RESULTS AND DISCUSSION

3.1 Age Model:

Sedimentation rates decreased significantly from 33 m/Myr in the upper Aptian to ~5.6 m/Myr in the Cenomanian with the lowest sedimentation rates (~5 m/Myr) in the middle to lower upper Albian interval (484.6 – 457.8 mbsf, 109.4 – 103.1 Ma). Sedimentation rates increased to 12.5 m/Myr in the uppermost Albian (455.7-424.29), but fell again to 5.6 m/Myr in the early Cenomanian. The highest sedimentation rates in the section (33.2 m/Myr) were found in the uppermost Aptian (543 – 530 mbsf, 113.4 – 113 Ma). The accuracy of the age model is lower in Cores 40X-41X due to the absence of a nannofossil datum below the base of *Seribiscutum primitivum* (113.4 Ma, 543.7 mbsf, Core 39X-CC). Sedimentation rates may be lower due to the higher abundance of clay content observed as a prominent color change in core 41X. The age model was used to convert depths of all samples to age (*Appendix Table 1*)
Figure 12. Left: Sedimentation rates generally decrease up-section through the Albian and lower Cenomanian. Right: A depth-age plot of all samples in the study using nannofossil event datums published in Braiower and Seisser, 1992. Datum ages are calibrated on the 2012 Geologic Time Scale [Gradstein et al., 2012]
3.2 Micropaleontology:

All mineral and biocomponents were classified into the following groups: planktic and benthic foraminifera, radiolarians, inoceramid prisms, and pyrite nodules. Planktic forams were further divided into keeled and non-keeled groups (Figures 13-1, 13-2). Benthic forams were split into eight primary genera: Osangularia, Gavelinella, Gyroidinoides, Gaudryina, Stensoina, Globorotalites, Lenticulina, and Dorothea (Figures 14-1, 14-2).

Different biocomponents dominate parts of the section starting with a sporadic dominance of planktic forams in the upper Aptian, 563.46 – 530.28 mbsf (113.99 – 113 Ma) followed by a marked abundance of benthic forams in the basal Albian at 528.73 mbsf (sample 37X-5, 112.94 Ma), which then decline significantly at 525.7 mbsf (112.7 Ma). Radiolarians dominate the lower Albian part of section between 519 – 503 mbsf (112.27 - 111.14 Ma) followed by pulses of abundant inoceramid prisms in the middle Albian between 489 – 437.02 mbsf (110.04 - 101.46 Ma). Pyrite and keeled planktic forams dominate the uppermost Albian part of the section between 446.7 – 425 mbsf (102.2 – 100.5 Ma).

Planktic forams are generally more abundant than benthics but their counts reveal rhythmic peaks in abundance every ~10 meters in the section. Benthic forams peak abundance was found in the lowest Albian sample in Core 37X-5 at 528.73 mbsf, (112.94 Ma), followed by a significant decline over the interval 528.73 – 492 mbsf. Changes in benthic foraminiferal abundance appear to correlate with changes in sedimentation rates and abundance of inoceramid prisms. Benthic taxonomy shows there are at least 3 horizons where abundances decrease in all taxa (530, 492, and 440 mbsf) (Figures 14-1 and 14-2).
Figure 13-1. Abundance data for all five major components vs depth (mbsf). Benthic foraminifera dominate the interval (530 – 525 mbsf) followed by a dominance of radiolarians (519 – 505 mbsf), followed by inoceramid prisms (490 – 455 mbsf) followed by pyrite and keeled planktics (455 – 425 msf)
Figure 13-2. Percentage data plotted against depth for all five major components, in addition to keeled planktics. Benthic and planktic percentages are present in the entire section and show apparently cyclic changes. Radiolarian percentages are high in the early Albian and early Cenomanian while Inoceramids often dominate the interval between the middle and late Albian. Pyrite and keeled planktic percentages dominate the uppermost late Albian.
Figure 14-1. Benthic foraminifera counts are dominated by eight main genera: Osangularia, Gavelinella, Gaudryina, Gyroidinoides, Dorothia, Globorotalites, Stensoina and Lenticulina. Most taxa appear at the Aptian/Albian boundary and show trends that lead to disappearance at 493 and 440 mbsf.
Figure 14-2. Benthic taxa percentage data plotted against age. Osangularia is the dominant benthic genera in the section but it is absent in the Aptian. On the other hand, Gavelinella, Gaudryina, Gyroidinoides, and Lenticulina are present in the Aptian and show increasing percentages up-section.
3.3 Isotope Stratigraphy

The isotopic composition of both epifaunal benthics, *Osangularia schloenbachi* and *Gavelinella* spp., is remarkably similar in both Carbon and Oxygen isotopes. The long-term trend of $\delta^{13}C$ isotopes of benthics and bulk fine-fraction (FF) gradually decrease upwards with sharp negative excursions in the upper half of the section. Oxygen isotopes of bulk FF gradually decrease upwards through the Albian, while benthic values are generally steady except for several negative excursions that coincide with carbon isotope excursions.

3.4 Isotopic composition

Carbon and Oxygen isotope values can be divided in four sections:

- **563 – 530 mbsf**
  Carbonate bulk fine fraction data was sampled at high-resolution, however, the isotopic values show dramatic variability in the upper Aptian part of the section. Planktic *Microhedbergella* and benthic *Gavelinella* were present in the upper part of this interval and their isotopic compositions are remarkably similar.

- **530 – 482 mbsf**
  A negative $\delta^{13}C$ excursion at 530 mbsf is typical of OAEs followed by an increased gradient in both carbon and oxygen isotopes between bulk FF and benthic forams suggesting a significant change in water column stratification and carbon cycling.

- **482 – 448 mbsf**
  Three synchronous high amplitude negative excursions occur in benthic and bulk FF except in bulk FF $\delta^{18}O$ where isotopic show positive excursions that coincide or lag benthic excursions. An opposite trend occurs between these high amplitude excursions.
where isotopic values and gradients increase.

- **448 – 410 mbsf**

The gradient between $\delta^{18}O$ values increases dramatically with increasingly depleted values of bulk FF while benthics are gradually more enriched. The gradient between $\delta^{13}C$ values also increases significantly, however, bulk FF values become more depleted up to 429 mbsf followed by steep enrichment up to 410 mbsf.

### 3.5 Temperature Calculations

The $\delta^{18}O$ of calcite is related to the $\delta^{18}O$ of the seawater from which it precipitated by a temperature and/or salinity factor. However, the effect of salinity on benthic $\delta^{18}O$ values is excluded in this site due to its 1000 m paleo-water depth during deposition, which reduces the effect of evaporation and precipitation. Temperature variations can be divided into the same four categories used to define isotopic values. Assuming $\delta^{18}O_{\text{seawater}} = -1\%$, bulk FF temperatures increase gradually from $\sim13^\circ$ to $24^\circ C$, while benthic temperature estimates increase from $\sim11^\circ$ to $15^\circ$ in the upper part of the section. Bottom water temperatures show positive excursions of up to $4^\circ C$ in the middle part of the section (Figure 16).

### 3.6 Isotopic Gradients

Isotopic gradients are the differences between isotope values of benthic foraminifera and mixed layer calcareous plankton illustrated in bulk FF, assumed to be largely composed of calcareous nannoplankton and juvenile planktic foraminifera. Gradients in $\delta^{13}C$ may explain local changes in primary productivity or changing surface or intermediate water masses, while $\delta^{18}O$ gradients represent changes in the thermocline and water column stratification.
Plots of both Carbon and Oxygen isotope gradients show three nadirs at 482, 467 and 451 mbsf. The carbon isotopic gradient collapses at the Aptian/Albian boundary at 530 mbsf while oxygen isotope gradients collapse above and below this horizon at 524 and 533 mbsf consecutively (Figure 17).
Figure 15. Isotope records for the study interval. Left: Carbon isotopes. *Osangularia* and *Gavelinella* values track each other very closely with a small offset in values. Benthic & bulk FF $\delta^{13}C$ values decrease gradually in the long term but several high amplitude excursions interrupt the record. $\delta^{18}O$ values.
Figure 16. Temperature estimates from oxygen isotopes show high variability up to 530 mbsf. Mixed layer temperatures increase gradually upwards with severe fluctuations in temperature between (492 – 448 mbsf). Benthic temperature estimates show slower temperature increases upwards interrupted by high amplitude warming events between (479 – 451 mbsf).

Figure 17. Carbon and Oxygen isotopic gradients between mixed layer calcareous nannoplankton represented by bulk fine fraction and deep waters represented by benthic foraminifera. Calcareous plankton and benthic foraminifera show three sharp excursions from 480-450 mbsf (gray bars), which coincide with benthic warming events (Figure 16). At 530 mbsf the $\delta^{13}$C gradient collapses while the $\delta^{18}$O gradient collapses above and below this horizon at 524 and 533 mbsf.
3.7 Chronostratigraphy

3.7.1 OAE1b Kilian Event (Aptian/Albian boundary)

The Aptian/Albian boundary is placed at a suspected unconformity between Sample 37X-5 (lowest Albian sample, 528.73 mbsf, 112.95 Ma) and 37X-6 (highest Aptian sample, 530.28 mbsf, 113.00 Ma). SEM images of planktic foraminifera show a significant change in taxonomy and surface ultrastructure between these two samples (Figure 18). The lowest occurrence of *Microhedbergella renialevis*, a lowermost Albian small, smooth, microperforate planktic foraminifera with four chambers in the final whorl occurs at 37X-5 and is preceded by poorly preserved planktic specimens in 37X-6. The Highest Occurrence of *Hedbergella infracretacea* is in the uppermost Aptian. This finely perforate taxon is covered by pore mounds on the shell surface, a characteristic feature of late Aptian species of *Hedbergella*. *Microhedbergella miniglobularis* has a narrow range straddling the Aptian/Albian boundary (uppermost Aptian *Mi. miniglobularis* zone, 113.26 Ma, to basal Albian *Mi. rischi* zone, ~112.4 Ma; Huber and Leckie, 2011; Petrizzo et al., 2012; Kennedy et al., 2014) and it occurs in both samples (37X-5 and 37X-6) further supporting the proximity of both samples to the Aptian/Albian boundary and suggesting that any break in the record was short.

A negative ~2.5‰ δ¹³C excursion occurs in benthic and bulk FF data at the highest Aptian sample 37X-6, 530.28 mbsf. This excursion correlates well with a negative 1.8‰ excursion between the *Mi. miniglobalitis* and *Mi. renialevis* zones in the proposed GSSP locality in the Col de Pré-Guittard section in the Vocontian basin, SE France [Petrizzo et al., 2012] (Figure 20). The abundance and preservation of planktic and benthic foraminifera changes drastically between 37X-5 and 37X-6 suggesting a dramatic shift in the paleoenvironment across the Aptian/Albian boundary.
Figure 18. SEM images of planktic forams reveal severe dissolution, or acidification(?) in the uppermost Aptian sample compared to the basal Albian sample. *Microhedbergella miniglobularis* occurs in both samples, showing poor preservation in the Aptian. *Hedbergella aptiana* and *Hedbergella infracretacea* are upper Aptian marker taxa. *Microhedbergella rischi* and *Mi. renilaevis* are both exclusively lower Albian taxa.
Figure 19. A comparison of the carbon isotope and planktic foraminifera records from the Vocontian Basin support the placement of the Aptian/Albian boundary at 530 mbsf. A negative carbon isotope excursion is observed in benthic and bulk fine fraction carbonates in ODP Hole 763B which coincides with the lowest occurrence of a zonal marker *Microhedbergella renilaevi*
3.7.2 The Albian Sub-stage and Albian/Cenomanian boundary

The early/middle Albian boundary (110.7 Ma) is placed at 489 mbsf, the middle/late Albian boundary (107.6 Ma) is placed at 476 mbsf, and the Albian/Cenomanian boundary (100.5 Ma) is placed at 425 mbsf based on the calcareous nannofossil-based age model for Site 763, and supported by planktic foraminiferal biostratigraphy. Plotting chronostratigraphic boundaries on a combined plot of isotope values, sedimentation rates, and biocomponent and mineral graphs reveals significant changes across OAE1b. In addition, the middle to upper Albian show an inverse correlation between isotope values and the abundance of inoceramid prisms. Pyrite nodules are more abundant in the uppermost Albian where isotope values stabilize and gradients become larger. The Albian/Cenomanian boundary coincides with a drop in planktic foraminifera and pyrite nodule abundances (Figure 20).
Figure 20. The Aptian/Albian boundary coincides with a negative excursion in carbon isotopes, increased abundance of benthic and planktic foraminifera, radiolarians, inoceramid prisms, and a significant decrease in sedimentation rates. The early Albian has the highest abundance of radiolarians while the middle and early late Albian coincide with sharp isotope excursions, slower sedimentation rates and increased abundance of benthic forams and inoceramid prisms. Pyrite nodule counts and the percentage of keeled planktics increase in the latest Albian coinciding with a severe decline in Inoceramid prisms, stabilized isotope values an increasing gradient.
3.8 Albian Oceanic Anoxic Events

The Niveau Kilian black shale represents the Aptian/Albian boundary in the Vocontian Basin of southeast France and it has been placed at sample 37X-6, 530.25 mbsf as discussed in the Chronostratigraphy section above. A table of numerical ages of Vocontian Basin black shale horizons based on (GTS 2012) are listed below.

Table 1. A list of globally established OAEs within the study interval. Numerical ages are based on the 2012 Geological Time Scale [Gradstein et al., 2012]

<table>
<thead>
<tr>
<th>Horizon</th>
<th>OAE designation</th>
<th>Age top</th>
<th>Age bottom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Niveau Breistroffer</td>
<td>OAE 1d</td>
<td>100.98</td>
<td>101.03</td>
</tr>
<tr>
<td>Niveau Amadeus</td>
<td>OAE 1c</td>
<td>106.78</td>
<td>107.18</td>
</tr>
<tr>
<td>Niveau Leenhardt</td>
<td>OAE 1b</td>
<td>110.23</td>
<td>110.28</td>
</tr>
<tr>
<td>Niveau Paquier</td>
<td>OAE 1b</td>
<td>111.15</td>
<td>111.27</td>
</tr>
<tr>
<td>Niveau Kilian</td>
<td>OAE 1b</td>
<td>113.02</td>
<td>113.14</td>
</tr>
</tbody>
</table>

All OAE horizons correspond with reduced abundances of planktic and benthic foraminifera, OAE ages were used to investigate sharp drops in foraminiferal abundances in Hole 763B. Indeed, a drop in planktic and/or benthic forams are observed within ~160 kyr in our age calibrated samples relative to established global ages of OAEs. The depths of horizons equivalent to OAEs are listed below including the calculated difference between Site 763 age model relative to globally established ages of OAEs.

Table 2. A list of the ages and depths of OAEs coinciding with severe drops in the total number of foraminifera. The Site 763 age model correlates to the Albian OAEs within ~0.16 myr.

<table>
<thead>
<tr>
<th>Horizon</th>
<th>OAE designation</th>
<th>Site 763 Depth</th>
<th>Standard Age (GTS 2012)</th>
<th>Site 763 Age Model</th>
<th>Difference in age (myr)</th>
<th>Total Forams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Niveau Breistroffer</td>
<td>OAE 1d</td>
<td>427.73</td>
<td>101.01</td>
<td>100.72</td>
<td>0.28</td>
<td>0</td>
</tr>
<tr>
<td>Niveau Amadeus</td>
<td>OAE 1c</td>
<td>475.09</td>
<td>106.98</td>
<td>107.26</td>
<td>-0.08</td>
<td>1784</td>
</tr>
<tr>
<td>Niveau Leenhardt</td>
<td>OAE 1b</td>
<td>493.73</td>
<td>110.26</td>
<td>110.47</td>
<td>-0.19</td>
<td>64</td>
</tr>
<tr>
<td>Niveau Paquier</td>
<td>OAE 1b</td>
<td>503.23</td>
<td>111.21</td>
<td>111.14</td>
<td>0.13</td>
<td>1456</td>
</tr>
<tr>
<td>Niveau Kilian</td>
<td>OAE 1b</td>
<td>530.25</td>
<td>113.08</td>
<td>113.00</td>
<td>0.14</td>
<td>3072</td>
</tr>
</tbody>
</table>

A plot of the total foraminifera counts (benthics and planktics) shows abrupt drops coinciding with globally established OAE horizons (Figure 20).
An additional observation is that, during OAEs, planktic abundances decline more sharply than radiolarian and benthic abundances resulting in lower planktic/radiolarian ratios (P/R) and planktic/benthic ratios (P/B) (Figure 22). This suggests that conditions associated with OAEs had a stronger effect on planktics than benthics and radiolarians, further suggesting that the water column over Site 763 on the Exmouth Plateau was not strictly anoxic. Anoxia on continental margins develops through increased upwelling resulting in higher productivity and expansion of the Oxygen Minimum Zone [OMZ; e.g., Takashima et al., 2006]. However, the presence of radiolarians during OAE events suggests the absence of a strong OMZ, hence, ocean acidification may have had a stronger factor on the abundance of planktic forams. Ocean acidification typically has a stronger effect on surface dwellers relative to deeper
ones causing a stronger biocalcification failure in the mixed layer relative to deeper sections of the water column [Erba et al., 2015]. The dominance of radiolarians over planktic forams in OAEs may suggest the presence of upper water column acidification as silica based protists are more resistant to ocean acidification.

Using the P/B and P/R ratios and the foraminifera number, eight additional acidification events may exist in the Albian section of ODP Site 763. The variable occurrence frequency of acidification events does not reflect systematic cyclicity as observed in plots of acidification events versus age (Figure 23). The poor preservation of upper Aptian sample 37X-6, 530.25 mbsf, is consistent with acidification due to temporal proximity with the correlative Kilian level.
Figure 22. All OAEs (except for Leenhardt), coincide with increased dominance of radiolarians and benthics over planktics. Ocean acidification may have caused severe biocalcification failure in the upper water column.
Figure 23. All OAEs may be associated with ocean acidification due to low foraminifera counts and P/B and P/R ratios. 13 acidification events, including 5 that correlate with OAEs are proposed for the study interval. All suggested acidification events do not occur on systematic cyclicity.
3.9 Paleoenvironment

3.9.1 Micropaleontology

A paleobathymetric model of Cretaceous benthic foraminifera from the Australian continental margin [Scheiberova, 1976] suggests the dominance of outer neritic to upper bathyal taxa in the studied interval of ODP Site 763 (Figure 24). The presence or absence of benthic genera from different bathymetric ranges can facilitate paleoenvironmental interpretations. For example, the absence of *Gaudryina*, an agglutinated benthic foraminifera exclusive to outer neritic settings may suggest the falling or rising sea levels depending on the changes in benthic assemblages. In addition, the exclusive presence of *Gyroidinoides*, a middle to bathyal calcareous benthic foraminifera, with inoceramid prisms in sample 33X-3, 487.7 mbsf, 110.04 Ma suggests a middle neritic environment for inoceramids due to the absence of all outer neritic and bathyal benthics. In addition, inoceramid prisms could also be outer neritic as the abundance of *Gaudryina* and inoceramid prisms decreased significantly between (467 – 468 mbsf, 105.37 – 105.75 Ma), despite an increase in benthic abundances overall, suggesting a co-habitation between *Gaudryina* and inoceramids (Figure 25). Therefore, the dominance or absence of inoceramid prisms may indicate changes in sea level, due to their inferred presence in neritic environments.

Infaunal benthic foraminifera can indicate low or high carbon fluxes based on observed adaptations of modern foraminifera and inferred preferences from similar geological settings in the same time interval [e.g., Holbourn, et al., 2001]. The percentage of *Dorothia oxycona* and *Gaudryina* (infaunal benthic foraminifera adapted to low carbon fluxes) increases upwards which is consistent with gradually decreasing values of δ13C and rising sea levels as bottom waters had lower organic carbon fluxes (Figure
Slower sedimentation rates and higher sea level are associated with higher benthic foraminifera abundances in the mid-late Albian (486 – 456 mbsf, 110 -113.12 Ma ) which coincides with the “inoceramid acme”. In addition, the abundance of inoceramid prisms is associated with a decline in radiolarians and planktic forams (Figure 27). Since inoceramid prisms indicate neritic environments, their abundance may reflect falling sea levels associated with a decline in planktic and radiolarian abundances and vice-a-versa.
Figure 24. A paleobathymetic model of benthic genera in the Australian margin suggests that most benthic foraminifera formed in outer neritic to upper bathyal marine conditions. Adapted from [Scheiberova et al., 1976]
Figure 25. Inoceramids indicate a middle to outer neritic bathymetry. A simultaneous decrease in *Gaudryina* and inoceramid prisms despite increasing benthic counts suggests rising sea levels and a decreasing influence of outer neritic components on the study interval. Inoceramids could also be middle neritic due to the exclusive presence of *Gyroidinoides* with inoceramids suggesting decreasing sea levels as all bathyal and outer neritic benthics disappear.
Figure 26. A gradual increase in infaunal benthics (*Gaudryina* and *Dorothia*) suggests lower oxygenation and increasing organic matter flux to the sea floor. This is consistent with a gradual decrease in benthic δ¹³C and rising mean sea levels.
Figure 27. The abundance of inoceramid prisms is associated with a decline in planktic and radiolarian abundances suggesting that inoceramid prisms may reflect changes in sea levels. Inoceramid prisms suggesting the development of neritic environments or downslope transport from neritic environments during a sea level fall.
3.9.2 Stable Isotope Record

- **563 – 530 mbsf (Upper Aptian)**

  The isotopic composition of late Aptian bulk FF samples is variable in both oxygen and carbon isotopes possibly due to the abundance of smectite muds, which can cause significant diagenetic variations in isotope compositions [Figure 15; Exon et al., 1992; Price et al., 2012]. However, SST estimates from bulk FF oxygen isotopes did not exceed 17°C while benthic temperature estimates did not exceed 14°C in Cores 41X-39X (563 – 543 mbsf, 114 – 113.4 Ma). Such low SST values are associated with the late Aptian cooling (116-114 Ma) and long-term low stand (118-113 Ma) [McAnena et al., 2013; Maurer et al., 2012].

  Core 38X (533 – 532 mbsf, 113.09 – 113.06 Ma) shows positive $\delta^{13}C$ excursion in benthic and bulk fine fraction values. However a positive $\delta^{18}O$ excursion occurs in the benthic and planktic record but not in bulk FF. A late Aptian transgression may coincide with this positive $\delta^{13}C$ excursion as suggested by Price (2012) in late Aptian $\delta^{13}C$ record of belemnites in the Carnarvon Basin, Australia.

- **530 – 482 mbsf (Lower to Middle Albian)**

  Samples 37X-6 and 37X-5 (530.25 and 528.75 mbsf) are the uppermost Aptian and lowermost Albian, respectively, as discussed in the Chronostratigraphy section. Oxygen isotopes of both samples show a cooling signal across the boundary and a brief recovery of ocean stratification associated with higher abundances of benthics, planktics, radiolarians, and inoceramid prisms at sample 37X-5. The Haq (2014) eustatic sea level curve suggests a falling sea level across the Aptian/Albian boundary, which may be consistent with a cooler temperatures seen in ODP Hole 763B. The high abundance and diversity of biocomponents in samples 37X-5 and 37X-4 may be part of a prograding
sequence during a sea level fall. On the other hand, increased biotic diversity and abundance may be produced from a high-order sea level rise in the earliest Albian within a generally regressive early Albian sequence (sea level discussion).

Reworking of late Aptian planktic forams has been observed by Huber and Leckie (2011), as Aptian species co-occur with early Albian forms as high as Sample 36X-CC (522.67 mbsf, 112.5 Ma). Lower abundance, severe dissolution and mixed δ¹⁸O signals are also observed in Osangularia through this interval of reworking (530.25 – 522.67 mbsf, 112.95 – 112.5 Ma). Reworking can be a feature of an early transgressive systems tract, while the abundance of radiolarians in the overlying interval (519 – 505 mbsf, 112.3 – 111.1 Ma) is more consistent with a late transgressive systems tract. Alternatively, downslope transport of benthic foraminifera is consistent with a significant sea level fall on a continental slope. Therefore, falling sea level may have reworked Aptian and early Albian benthic and planktic forams from neritic to upper bathyal settings.

Oxygen isotope gradients increase and stabilize between (505 – 492 mbsf, 111.1 – 110.4) which, combined with the dominance of radiolarians, suggests a late transgressive and highstand sequence with normal marine stratification. This is followed by a falling sea level between (492-482 mbsf, 110.2 -109.1 Ma) as suggested from higher abundances of inoceramid prisms and Gyroidinoides deposited in a middle to outer neritic environment. Temperature estimates suggest that the benthic realm warmed by ~4°C in an interval (492 – 482 mbsf, 100.2 – 109.1 Ma) where inoceramid prisms decrease.

- **482 – 448 mbsf (Middle to Upper Albian)**

Oxygen and Carbon isotope gradients decline significantly in three pulses at (479, 467 and 451 mbsf, 108.37, 105.4 and 102.6 Ma). An important observation is the increased
abundance of planktic, benthic, and radiolarians coincide with increased water column mixing as indicated by the lower temperature gradients indicated by lower oxygen isotope gradients. Negative carbon excursions in both benthic and bulk FF suggest an upwelling signal and increased productivity, but not an OAE. Typical upwelling events are associated with negative carbon excursions in benthic and planktic foraminifera due to the influence of $^{13}$C depleted, nutrient-rich waters [Pak and Kennett, 2002].

The coincidence of upwelling with increasing abundances of radiolarians and planktic forams with rising sea levels interpreted based on a decline in inoceramid prisms suggests a causal effect. Three pulses of warmer bottom waters suggest a sea level controlled invasion of temperate, nutrient-rich water masses in the middle to early late Albian affecting Site 763. Perhaps these warming pulses are due to the production of warm, saline intermediate waters along the subtropical northern margin of Australia. In addition, carbon and oxygen isotope gradients increase and cooler temperatures alternate with the warming events, and coincide with increased inoceramid prism abundances and falling sea level.

A strong correlation between oxygen isotopes and 3rd order eustatic sea level cycles has been observed in a long ranging Cretaceous record in the Contessa section in Italy [Haq, 2014]. The time interval between the three oxygen isotope excursions at (108.37, 105.4 and 102.6 are 2.98 and 2.74 Ma consecutively which is typical of 3rd order eustatic sea level cycles which can range from 0.5 to 3 myr [Haq, 2014]. Therefore, 3rd order eustatic cycles resulted in invasion of warmer bottom waters, decreased stratification, increased upwelling and higher planktic and radiolarians populations during transgressions. Regressions resulted in cooling, increased inoceramids on the shelf, increased stratification and decreased abundance of planktic and radiolarian populations.
• **448 – 410 mbsf (Uppermost Albian)**

Carbon and oxygen isotope gradients achieve the largest values in the uppermost Albian, indicating the strongest water column stratification in the studied section. Pyrite nodules become dominant in the interval (447 – 425 mbsf, 102.2 – 100.5 Ma) suggesting the development of euxinic conditions on the seafloor and in the water column as planktic, benthic, and radiolarian populations are almost absent. Despite the high abundance of pyrite in several samples, euxinic conditions may have only formed in two horizons, one of which coincides with OAE1d placed at 427.73 mbsf, 100.74 Ma and the other at 440 mbsf, 101.7 Ma. The presence of euxinia in an intensely stratified water column suggests that higher sea levels in the late Albian were associated with bottom water anoxia possibly caused by increased rainfall and decreased salinity in surface waters resulting in a weakened ocean circulation [Wilson and Norris, 2001; Bornemann et al., 2005].

The Albian/Cenomanian boundary placed at (425 mbsf, 100.5 Ma) coincides with an abrupt decline in planktic abundances and pyrite nodules, while radiolarian abundances increase possibly due to increased acidification. The Albian/Cenomanian boundary shows no decline in water column stratification resulting in a similar susceptibility to bottom water anoxia and/or euxinia. However, the lack of pyrite and increased frequency of acidification events may have reduced the presence of organic matter and subsequent H₂S resulting in decreased abundances of pyrite. A decline in organic matter, implied from a decline in pyrite, suggests that limited nutrients may have caused a decline in planktic abundances and an increase in radiolarians, in addition, to acidification possibly caused by the formation of the central Kerguelen Plateau starting in 102 Ma (www.ga.gov.au, retrieved November 2015).

A Tethyan influence is inferred in the interval between (456 – 413 mbsf, 103 – 98.5
Ma) based on the incursion of keeled planktic foraminiferal taxa, including *Planomalina buxtorfi* and species of *Rotalipora* and *Praeglobotruncana*, which are typical of low latitudes [Caron, 1985, 1989; Premoli Silva and Sliter, 1999]. In addition, the dominance of heavily calcified, keeled planktics indicate the development of a deep thermocline indicating further stratification in the upper water column [Wilson and Norris, 2001; Leckie et al., 2002].
Figure 28. A composite plot of isotope data and mineral and biocomponents with sequence stratigraphic interpretations. The abundance of neritic inoceramid prisms associated with a cooler, more stratified water column indicates falling sea levels and increased delivery from neritic environments into bathyal settings. Increased abundances of planktic and radiolarian populations associated with decreased gradients, increased upwelling and negative carbon excursions are probably caused by rising sea levels which lead to the invasion of warmer bottom waters which increase upwelling.
Figure 29. A composite plot of isotope, mineral and biocomponent data with acidification events. Two horizons with euxinic conditions, one of which is OAE1d, replace two acidification events as the abundance of pyrite and lack of planktic, benthic and radiolarian populations suggests severe anoxia. The presence of deep thermocline keeled planktics and increased temperature stratification in δ¹⁸O values from the late Albian (112.6 Ma) to early Cenomanian suggest slower ocean circulation assisting the development of euxinic conditions.
3.10 Comparison of Isotope Records of Bulk Carbonate to Bulk Fine Fraction Carbonates and Benthic Foraminifera

A bulk carbonate oxygen isotope record from the Aptian-Cenomanian interval from Site 763B published by Clarke et al., 1999, is compared to the bulk fine fraction and benthic foraminifera isotope data generated in this study. Carbon isotope data of bulk carbonates was not previously published, but was provided by Dr. Leon Clarke (MMU) for comparison with data produced from this study. Bulk fine fraction data can be more representative of the mixed layer and photic zone compared to bulk carbonates because of a presumed greater concentration of autotrophic calcareous nanofossils and fewer heterotrophic planktic and benthic foraminifera. Therefore, the bulk fine fraction is expected to be more enriched in $\delta^{13}$C and more depleted in $\delta^{18}$O [Reghellin et al., 2015]. Indeed, our bulk fine fraction records were slightly more enriched in $\delta^{13}$C, but significantly more depleted in $\delta^{18}$O compared to Clarke’s bulk carbonate data.

3.10.1 Carbon Isotopes

Clarke’s bulk carbonate $\delta^{13}$C values are remarkably similar to our bulk fine fraction values, while $\delta^{18}$O values show a larger offset that increases in the upper Albian and Cenomanian. However, despite the similarity of the two carbon isotope time-series, which both record Excursions 2, 3 and 4, there are two excursions (5 and 6) that only show up in the bulk carbonate data (Figure 30). Perhaps Excursions 5 and 6 were short-lived and not represented in the fine fraction analyses of this study. The time difference between Excursions 5 and 6 suggests third-order cyclicity.
similar to the earlier Excursions 2, 3 and 4 in the middle to upper Albian. An additional difference in the two C-isotope time-series is that Clarke’s bulk carbonate data do not record a prominent negative excursion at the Aptian/Albian boundary (530 mbsf, Excursion 1) probably due to his lower sampling resolution near the boundary interval, which contains a 1-m sampling gap between the lowest Albian sample at 529.24 mbsf and the boundary at 530.28 mbsf.

3.10.2 Oxygen Isotopes

Clarke’s bulk carbonate $\delta^{18}O$ values are more enriched than our bulk fine fraction data, which is consistent with the likely greater presence of benthic foraminifera that formed in deeper, cooler water settings resulting in more enriched values. The sieving process of the bulk fine fraction samples removes a greater proportion of benthic and planktic foraminifera thereby concentrating the calcareous nannofossils and resulting in slightly more depleted $\delta^{18}O$ values compared to unsieved bulk carbonates.

The Aptian/Albian boundary (530 mbsf, Excursion 1) shows a prominent and simultaneous positive excursion in the $\delta^{18}O$ record of benthic and bulk fine fraction carbonate values suggesting significant bottom water cooling across the boundary and into the early Albian. This is consistent with cooling temperature trends from an oxygen-isotope study of belemnite guards from the lower Albian Gearle Siltstone of the Carnarvon Basin of western Australia, paleolatitude 40-45°S [Williamson, 2006]. However, oxygen isotope values of the Aptian/Albian boundary Niveau Kilian in the Vocontian basin exhibit a warming trend [Petrizzo et al., 2012; Huber et al., 2011]. On
the other hand, the dominance of terrestrial organic matter within Kilian in the Vocontian Basin of southeast France suggests a falling sea level facilitating the delivery of terrestrial organic matter into a marine setting [Herrle, 2003; Herrle, 2004; Okano, 2008]. In addition, correlative Kilian level angular quartz-rich turbidites were found within hemipelagic sediments in the deep Newfoundland Basin suggesting falling sea levels [Trabucho et al., 2011].

Clarke’s bulk $\delta^{18}O$ shows three excursions that coincide with benthic $\delta^{18}O$ excursions (2, 3 and 4). However, bulk fine fraction $\delta^{18}O$ excursions are variable; Excursion 3 is positive while excursions 2 and 4 are negative. In addition, excursion 2 has two negative prongs; one coincides with the benthic excursion and the other coincides with bulk fine fraction excursion. The presence of two excursions in bulk carbonate $\delta^{18}O$ isotopes indicates the validity of both excursions and confirms the presence of a vertical offset between benthic and bulk fine fraction excursions. Therefore, bulk carbonate $\delta^{18}O$ values could reflect excursions in the benthic or planktic realms or both. In addition, bulk carbonate $\delta^{18}O$ values show a smaller excursion than benthic and bulk fine fraction values suggesting that bulk $\delta^{18}O$ values may reflect an average of the benthic and planktic realms.

The increased offset between bulk and bulk fine fraction $\delta^{18}O$ values in the interval between 447 to 410 mbsf (uppermost Albian and lower Cenomanian) coincides with a significant increase in the abundance of deeper dwelling keeled planktic taxa, which are more enriched than typical mixed layer nannofossils [Reghellin et al., 2015] (Figure 31). Therefore, bulk carbonates generally represent mixed layer nannofossils, however, benthic and deep dwelling planktic foraminifera
may have a significant impact on the isotopic composition of bulk carbonates at a
time when tropical-subtropical thermocline taxa invaded the high southern
latitudes due to global warming and higher sea level during latest Albian time [e.g.,
Leckie et al., 2002].
Figure 30. A composite record of data produced in this study compared with Clarke’s bulk carbonate isotope values. The $\delta^{13}C$ values correlate well except for Excursion 1 at the Aptian/Albian boundary showing an attenuated excursion in bulk carbonates, while Excursions 5 and 6 are only prominent in bulk carbonates. Bulk carbonate oxygen isotope values are more enriched than bulk fine fraction values due to the presence of benthic foraminifera from a colder and deeper setting. A positive $\delta^{18}O$ excursion at the Aptian/Albian boundary (Excursion 1) supports the presence of cooler benthic conditions while bulk fine fraction data suggest generally cooler conditions during the latest Aptian compared with an overall warming during the Albian.
Figure 31. Clarke’s bulk isotope data are plotted with bulk fine fraction data from this study. Bulk fine fraction values are generally more enriched in $\delta^{13}C$ values and more depleted $\delta^{18}O$ values than bulk carbonates. The gradient between bulk and bulk fine fraction carbonates is mostly due to the presence of benthics in Clarke’s bulk carbonate records. However, the gradient is larger in $\delta^{18}O$ values and increases significantly between 448 and
3.11 Paleoenvironment across the Aptian/Albian OAE1b.

Negative carbon isotope excursions were observed in bulk carbonates and organic matter from the Niveau Kilian black shale in the Vocontian Basin, and from correlative black shales on the Mazagan Plateau and in the deep Newfoundland Basin [Herrle et al., 2004; Alexandre, 2011] (Figure 32). Negative excursions may be caused by a rapid reduction in productivity or an abrupt global change in the carbon cycle due to the input of isotopically light carbon from terrestrial organic matter, volcanogenic carbon dioxide, and/or the liberation of methane from methane hydrates. Volcanic eruptions can produce massive amounts of CO₂, which typically has a carbon isotopic composition between -2 to -6‰ [Faure & Mensing, 2005]. Methane, on the other hand, is much more depleted than carbon dioxide with carbon isotope values reaching -60‰ for biogenic sources and -40‰ for thermogenic sources [Faure and Mensing, 2005]. The implication is that it would take much less methane injected into the ocean-atmosphere system to cause a negative C-isotope excursion than if caused by volcanism [e.g., Dickens et al., 1995; DeConto et al., 2012].

The depleted isotopic composition of carbon dioxide is incorporated in calcite through the interaction of atmospheric CO₂ with seawater molecules forming depleted bicarbonate ions, which in turn combines with calcium ions forming depleted calcium carbonate:

1. \( \text{CO}_2(aq) + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{HCO}_3^- \)

2. \( \text{HCO}_3^- + \text{Ca}^{2+} \rightarrow \text{CaCO}_3 + \text{CO}_2(aq) + \text{H}_2\text{O} \)
Methane hydrates form along productive continental margins due to the decay of organic matter by methanogenic bacteria under relatively high pressure and low temperatures. Methane may be liberated from its solid hydrate form to a gaseous form if methane hydrates are destabilized by warmer deep or intermediate waters, which may have formed during the warmer Cretaceous climates [e.g., Thierstein and Berger, 1978; Brass et al., 1982; Arthur et al., 1987; Schmidt and Mysak, 1996]. Methane may react with dissolved oxygen in the water column forming heavily depleted CO₂.

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2^{(aq)} + 2\text{H}_2\text{O}
\]

The presence of negative C-isotope excursions in black shale equivalent to the Aptian/Albian boundary Niveau Kilian suggests that while primary productivity may have increased during the deposition of black shales, the effect of isotopically light carbon supersedes carbon isotope enrichment caused by elevated primary productivity and burial in the sedimentary record. In addition, the Kilian interval may have been dominated by eroded isotopically depleted terrestrial organic matter type III, which may produce negative isotope excursions. However, the presence of a negative carbon isotope excursion across the Aptian/Albian boundary in ODP Hole 763B suggests that in the absence of organic matter-rich black shale, the observed negative excursion is more likely due to changes in the global budget of carbon isotopes.
Figure 32. The Aptian/Albian boundary Niveau Kilian black shale in the Vocontian Basin (lower middle plot) and equivalent horizons in the Mazagan Plateau (lower right) and the Newfoundland Basin (left) show negative excursions due to the input of isotopically light carbon from a combination of possible sources, including volcanogenic CO2 associated with Kerguelen Plateau volcanism, liberation of methane hydrates due to rising bottom water temperatures, and/or erosion of terrestrial organic due to falling sea level. (Figure from Alexandre et al., 2011).
3.12 Late Aptian Cooling

Cooling during the late Aptian has been described by many authors [e.g., *Lini and Weissert*, 1991; *Mutterlose et al.*, 2009; *McAnena et al.*, 2013]. The most recent complete record of late Aptian cooling was published by Bottini et al., 2015 showing two phases of cooling, the first in the early late Aptian following OAE1a, and the second in the latest Aptian preceding the Aptian/Albian boundary. Temperature estimates from oxygen isotopes of bulk fine fraction samples from ODP Hole 763B show temperature ranges that vary between 11° – 16°C with warmer temperatures closer to the Aptian/Albian boundary. Despite the likely diagenetic alteration of oxygen isotope values and significant core gaps, the range of temperatures is much cooler than typical Cretaceous sea surface temperatures [e.g., *Norris and Wilson*, 1998; *Huber et al.*, 2002; *Leckie et al.*, 2002; *Friedrich et al.*, 2012].

3.13 Pyrite and Siderite as Expressions of Anoxia

The abundance of siderite (FeCO₃) and pyrite (FeS₂) may indicate that intensified anoxia developed sporadically in the late Aptian and latest Albian along the margin of northwest Australia. Siderite is abundant in the upper Aptian during prolonged low-stand sea level, while pyrite formed in the uppermost Albian when sea levels were significantly higher. Both minerals require the presence of organic matter and Fe(III), which may be have been supplied by hydrothermal fluids in the late Aptian and late Albian during the formation of the southern Kerguelen Plateau (119 – 110 Ma) and central Kerguelen Plateau starting around 102 Ma [*Leckie et al.*, 2002; *Erba et al.*, 2015].
Hydrothermal Fe(II) can be removed from solution if sulfides (HS⁻ and H₂S) are abundant in the water column, due to increased degradation of organic matter, resulting in the production of insoluble iron sulfide; pyrite (FeS₂) [Kendall, 2012].

\[
\text{Fe}^{2+} + \text{HS} \rightarrow \text{FeS} + \text{H}^+ \\
\text{FeS} + \text{H}_2\text{S} \rightarrow \text{FeS}_2 + \text{H}_2
\]

However, when hydrothermal Fe(II) concentrations exceed sulfide, iron may oxidize to Fe(III) in surface waters, followed by hydrolysis forming Fe(OH)₃ and in turn (FeCO₃) in the presence of organic matter in reducing conditions [Kendall et al., 2012; Kohler et al, 2013] (Figure 35)

\[
4\text{Fe(OH)}_3 + \text{CH}_2\text{O} \rightarrow \text{FeCO}_3 + 3\text{Fe}^{2+} + 6\text{OH} + 4\text{H}_2\text{O}
\]
Figure 35. Hydrothermal activity associated with the Southern Kerguelen Plateau could theoretically have supplied large amounts of Fe(II) in the late Aptian, which oxidized in shallower environments forming Fe(III), followed by hydrolysis forming Fe(OH)$_3$ and sinking to the ocean floor. Under anoxic conditions, Fe(OH)$_3$ can react with organic matter forming siderite. (Figures from Kendall et al., 2012 and Kohler et al., 2013).
CHAPTER 4
CONCLUSIONS

The late Aptian cooling may have affected the Site 763B as suggested by sea surface temperatures (~11° - 16°) calculated from oxygen isotope values of bulk fine fraction carbonates. The variability of oxygen isotope values suggests a diagenetic influence, however, the temperature range is significantly lower than typical Cretaceous sea surface temperatures. A 5-myr glacioeustatic (?) lowstand in the late Aptian may have assisted the development of siderite under anoxic conditions on the continental slope as hydrothermal fluids from the southern Kerguelen hotspot supplied iron that reacted with organic matter forming iron carbonate (siderite).

The Aptian/Albian boundary and the correlative Niveau Kilian black shale can be identified by a prominent negative C-isotope excursion, the disappearance of pore mound Aptian planktic foraminiferal ultrastructure, and the lowest occurrence of \textit{Microhedbergella renilaevis} and \textit{Mi. rischi}. The absence of organic matter-rich black shale associated with the correlative Kilian suggests that a negative carbon isotope excursion can be observed in carbonates due to the introduction of isotopically light volcanogenic CO$_2$, terrestrial organic matter, and/or methane. Carbon isotope excursions were not observed in other OAE1b (lower Albian) black shale equivalents; Niveau Paquier and Niveau Leenhardt. However, the correlative Paquier and Leenhardt levels coincided with severe ocean acidification based on the severe reduction in the number of foraminifera, in general, and planktic foraminifera, in particular, and the dominance of radiolarians in the upper water column. Ocean acidification also coincides with correlative upper Albian OAE1c and 1d levels, in addition to several horizons, not typically associated with Albian oceanic anoxic. Therefore, ocean acidification may have occurred more frequently in the mid-Cretaceous than oceanic anoxic events. Ocean
acidification probably occurred due to the enhanced production of volcanogenic carbon
dioxide from the Kerguelen Plateau and other sources.

The Albian interval in ODP Hole 763B contains an assemblages of benthic
foraminifera that suggest a wide paleobathymetric range from middle neritic (100 m) to
upper bathyal (600 m) water depths. However, cycles of abundant inoceramid prisms,
which may have proliferated in strictly neritic paleobathymetric zones, are used to infer
third-order sea level cycles. In addition, inoceramid prisms were abundant during
cycles of cooler and more stratified water columns, which may have been associated
with falling sea levels leading to the redeposition of neritic inoceramids on the
continental slope. In addition, inoceramid prisms decrease abruptly during rising sea
levels leading to the invasion of warmer subtropical intermediate waters causing
enhanced upwelling. Upwelling is inferred from reduced oxygen isotope gradients
interpreted as weaker temperature stratification of the water column. Upwelling is also
evident in lower carbon isotope gradients between benthic foraminifera and bulk fine
fraction values as upwelling supplies isotopically depleted nutrients to surface waters
leading to negative excursions in both benthic foraminifera and bulk fine fraction.

The lates Albian – early Cenomanian interval exhibits the appearance of and
alternating dominance between thermocline dwelling keeled planktic foraminifera and
pyrite nodules. Keeled planktic foraminfera indicate the influence of a war, Tethyan
water mass and the development of a deep thermocline while pyrite may have been
deposited under euxinic conditions during intensified stratification. Both
interpretations can be consistent with globally rising sea levels in the middle
Cretaceous.

Comparison of bulk and bulk fine fraction carbon isotope values indicates
remarkably similar values while oxygen isotopes are more enriched than bulk
carbonates values. The depleted values of bulk carbonates suggest the influence of depleted benthic foraminifera, which were eliminated from the fine fraction during the sieving process. The offset between bulk and bulk fine fraction oxygen isotope values increases in the late Albian to early Cenomanian, which is consistent with the presence of thermocline dwelling keeled planktic foraminifera in bulk carbonates.

Siderite and pyrite represent expressions of anoxia during intensified stratification associated with the late Aptian lowstand and the late Albian transgression. The formation of both minerals requires anoxia and the presence of hydrothermal iron, which may have been supplied by the South Kerguelen (late Aptian-early Albian) and Central Kerguelen (late Albian) hotspot volcanism, respectively.
## APPENDIX

### AGE MODEL RESULTS

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