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Lower Aptian Comparative Stratigraphy of the Basco-Cantabrian Region (Spain) and Eastern Cordillera (Colombia): implications for local factors in the depositional record of Oceanic Anoxic Event 1a (OAE-1a)

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

LOWER APTIAN COMPARATIVE STRATIGRAPHY OF THE BASCO-CANTABRIAN
REGION (SPAIN) AND EASTERN CORDILLERA (COLOMBIA): IMPLICATIONS FOR
LOCAL FACTORS IN THE DEPOSITIONAL RECORD OF OCEANIC ANOXIC EVENT 1A
(OAE-1A)

A dissertation submitted in partial fulfillment of

the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

GEOSCIENCES

by

Tatiana Gaona-Narvaez

2013

To: Dean Kenneth G. Furton
College of Arts and Sciences

This dissertation, written by Tatiana Gaona-Narvaez, and entitled Lower Aptian Comparative Stratigraphy of the Basco-Cantabrian Region (Spain) and Eastern Cordillera (Colombia): implications for local factors in the depositional record of Oceanic Anoxic Event 1a (OAE-1a), having been approved in respect to style and intellectual content, is referred to you for judgment.

We have read this dissertation and recommend that it be approved.

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The dissertation of Tatiana Gaona-Narvaez is approved.

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University Graduate School

Florida International University, 2013

DEDICATION

To my parents, for a whole life of love and support.

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ABSTRACT OF THE DISSERTATION

LOWER APTIAN COMPARATIVE STRATIGRAPHY OF THE BASCO-CANTABRIAN REGION (SPAIN) AND EASTERN CORDILLERA (COLOMBIA): IMPLICATIONS FOR LOCAL FACTORS IN THE DEPOSITIONAL RECORD OF OCEANIC ANOXIC EVENT 1A (OAE-1A)

by

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An important episode of carbon sequestration, Oceanic Anoxic Event 1a (OAE-1a), characterizes the Lower Aptian worldwide, and is mostly known from deeper-water settings. The present work of two Lower Aptian deposits, Madotz (N Spain) and Curití Quarry (Colombia), is a multiproxy study that includes fossil assemblages, microfacies, X-ray diffraction bulk and clay mineralogy, elemental analyses (major, minor, trace elements), Rock-Eval pyrolysis, biomarkers, inorganic and organic carbon content, and stable carbon isotopes. The results provide baseline evidence of the local and global controlling environmental factors influencing OAE-1a in shallow-water settings. The data also improve our general understanding of the conditions under which organic-carbon-rich deposits accumulate.

The sequence at Madotz includes four intervals (Unit 1; Subunits 2a, 2b and 2c) that overlap the times prior to, during and after the occurrence of OAE-1a. The Lower Unit 1 (3m thick) is essentially siliciclastic, and Subunit 2a (20m) contains Urgonian carbonate facies that document abruptly changing platform conditions prior to OAE-1a. Subunit 2b (24.4 m) is a mixed carbonate-siliciclastic facies with orbitolinid-rich levels that coincides with OAE-1a $\delta^{13}\text{C}$ stages C4-C6, and is coeval with the upper part of the *Deshayesites forbesi* ammonite zone. Levels with

pyrite and the highest TOC values (0.4-0.97%), interpreted as accumulating under suboxic conditions, and are restricted to $\delta^{13}\text{C}$ stages C4 and C5. The best development of the suboxic facies is at the level representing the peak of the transgression. Subunit 2c, within $\delta^{13}\text{C}$ stage C7, shows a return of the Urganian facies.

The 23.35-m section at Curití includes a 6.3-m interval at the base of the Paja Formation dominated by organic-rich marlstones and shales lacking benthic fossils and bioturbation, with TOC values as high as 8.84%. The interval overlies a level containing reworked and phosphatized assemblages of middle Barremian to lowest Aptian ammonites. The range of values and the overall pattern of the $\delta^{13}\text{C}_{\text{org}}$ (-22.05‰ to -20.47‰) in the 6.3m-interval is comparable with Lower Aptian $\delta^{13}\text{C}$ stage C7. Thus, conditions of oxygen depletion at this site also occurred after Oceanic Anoxic Event-1a, which developed between carbon isotope stages C3 and C6. Both sites, Madotz and Curití, attest to the importance of terrigenous and nutrient fluxes in increasing OM productivity that led to episodic oxygen deficiency.

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ABBREVIATIONS AND ACRONYMS

Al	Aluminum
Alb	Albian
Apt	Aptian
As	Arsenic
Ba	Barium
Bar	Barremian
C	Carbon
Ca	Calcium
CaCO ₃	calcium carbonate
cf.	<i>confer</i> meaning compare, consult
cm/kyr	centimeters per thousand years
Co	Cobalt
CO ₂	carbon dioxide
CPI	Carbon Preference Index
Cr	Chromium
e.g.	<i>exempli gratia</i> , meaning for example
EA-IRMS	Elemental Analyzer-Isotope Ratio Mass Spectrometer
EOM	Extracted Organic Matter
et al.	<i>et alii</i> , meaning and others
Fe	Iron
FID	Flame Ionization Detector
Fm	Formation
G	Gram

GC	Gras Chromatography
GC-MS	Gas Chromatography-Mass Spectrometry
HI	Hydrogen Index
HST	Highstand System Tract
K	Potassium
kyr	thousand years
LA-ICP-MS	Laser Ablation Inductively Coupled Plasma Mass Spectrometry
LECO	LECO Corporation; St. Joseph, Michigan
LST	Lowstand System Tract
Ma	Million years
Mg	Magnesium
mg	Milligram; $1 \text{ mg} = 10^{-3} \text{ g}$
min	Minute
ml	Milliliters; $1 \text{ ml} = 10^{-3} \text{ l}$
mm	millimeter; $1 \text{ mm} = 10^{-3} \text{ m}$
Mn	Manganese
Mo	Mmolybdenum
MSD	Mass Selective Detector
Na	Sodium
Ni	Nickel
Ni	Nickel
NIST	National Institute of Standards and Technology
O	Oxygen
OAE's	Oceanic Anoxic Events
OAE-1a	Oceanic Anoxic Event 1a

OC	Organic Carbon
OI	Oxygen Index
OM	Organic Matter
Org	Organic
P	Phosphorus
p.	Page
PDB	PeeDee Belemnite; from PeeDee Formation, South Carolina
ppm	Part per million; 10,000 ppm = 1 wt%
RE	RockEval Pyrolysis
SB	Sequence Boundary
Sc	Scandium
SEM-EDS	Scanning Electron Microscopy – Energy Dispersive Spectrometer
SIM	Selected Ionin Monitoring
SMR	Standard Reference Material
sp.	Species
Th	Thorium
Ti	Titanium
TIC	Total Inorganic Carbon Content
TMB	Tablazo-Magdalena Basin
TOC	Total Organic Carbon Content
TST	Transgressive System Tract
U	Uranium
V	Vanadium
XRD	X-Ray Diffraction
Zn	Zinc

$\delta^{13}\text{C}_{\text{org}}$

Carbon stable isotopes on bulk organic matter

μm

Micrometer or micron; $1\ \mu\text{m} = 10^{-6}\ \text{m}$

1 INTRODUCTION

The Cretaceous greenhouse climate produced widespread marine black shales rich in organic matter (OM), commonly related to pervasive Oceanic Anoxic Events (OAE's; Schlanger & Jenkyns, 1976). The C_{org} -rich deposits also include distinct positive excursions of stable carbon isotopes indicative of serious perturbations in the global carbon cycle (Ando, 2002, Jenkyns, 2010) related to high organic carbon productivity (Dumitrescu & Brassell 2005; Luciani et al. 2006; de Gea et al. 2008b; Heldt et al. 2008). Because these events generated deposits with high potential as hydrocarbon source rocks, and they can be used as possible analog models predictive of the consequences of high global temperature increases in the oceans, OAE's remain a major subject of interest and research.

Schlanger & Jenkyns (1976) interpreted the worldwide occurrence of Barremian-Aptian organic-rich marine sediments in the context of an oceanic anoxic episode named "Oceanic Anoxic Event 1" (OAE-1). Subsequently, a specific episode of anoxia was identified in the Lower Aptian (Oceanic Anoxic Event 1a, OAE-1a; Arthur et al., 1990) with duration of 1.0 to 1.3 Ma Li et al. 2008). OAE-1a has been associated with deposits of C_{org} rich sediments in multiple locations of the Tethyan Mediterranean region, Northern Europe, Russian Platform, North America and Mexico, as well as in the Pacific. In Europe these C_{org} deposits are known by regional names such as "Livello Selli" in the Umbria-Marche, and the Apennines of Northern Italy, and "Niveau Goguel" in the Vocontian Basin (Southern France). Despite much research, most of the works about sedimentology, geochemical and paleontological expressions of OAE-1a focus on pelagic and hemipelagic settings; recently the interest on the stratigraphic equivalents of OAE-1a in marine shallow water settings has risen (e.g. Vahrenkamp, 1996; Immenhausen, 2005; Föllmi & Gainon, 2008; Najarro et al., 2011; Huck et al., 2010). In shallow water settings, organic-carbon-rich facies may be inconspicuous, as diagnostic index fossils are scarce or absent, and geochemical proxies are unclear, thus leading to uncertainties concerning the exact temporal

assignment of the event. In addition, the extensive literature on Lower Aptian sedimentary successions reveals that contrasting facies development with varying amounts of organic carbon characterizes different areas, which suggests that both facies and organic matter accumulation were strongly controlled by local conditions (position of the section on the bathymetric profile, paleophysiography of the basin, local ecological limiting factors) superimposed on global forcing factors.

1.1 Biostratigraphy and Chemostratigraphy of Aptian Anoxic Events

The precise correlation of OAE-1a with ammonite and planktonic foraminiferal biozonations is still source of debate because the local results may be affected by different types of bias such as the absence of reliable index taxa as consequence of environmental or taphonomic factors, taxonomic misinterpretation of poorly preserved materials, and inconsistencies in the use of the bioevents used to mark the base of the biozones. In my dissertation I have adopted a stratigraphic position for OAE-1a, in the upper part of the *Deshayesites forbesi* ammonite Zone, on the basis of most recent works in sequences of the European Tethys (Moreno-Bedmar et al. 2009; Moreno-Bedmar et al. 2010; Moreno-Bedmar et al. 2012; Reboulet et al. 2012; Gaona-Narvaez et al, 2013a or Chapter 4 herein), Figure 1–2.

The geochemical signal that characterizes OAE-1a is commonly identified by comparison with stable carbon isotope curves showing distinct patterns labeled as C-segments developed on two pelagic successions of the Swiss Prealps, and the Southern Alps of northern Italy (Cismon and Roter Sattel sections; Menegatti et al., 1998), Figure 1–1. Worldwide Lower Aptian geochemical and biostratigraphic data related to OAE-1a demonstrate the following succession of events:

- A crisis in the plankton communities (“nannoconid crisis”) prior to OAE-1a (Erba, 1994).
The Nannoconid crisis starts at the top of carbon isotope segment C2 (e.g. Menegatti et al., 1998; Luciani et al., 2006), and has been argued to be a response to surface-water

acidification, and to be the cause of a drop in the sedimentation of nannofossil ooze in pelagic environments at that time (Erba, 1994; Erba et al., 2010)

Figure 1-1 Stable carbon isotope stratigraphy in the Italian Cismon section, after Menegatti et al. (1998).

- A brief negative $\delta^{13}\text{C}$ excursion (segment C3 of Menegatti et al., 1998; Figure 1–1) prior to OAE-1a presumed to be either associated with an abrupt release and oxidation of methane gas hydrates (Jenkyns, 2003; Renard et al., 2005; Méhay et al. 2009), or to increased volcanism (Méhay et al. 2009; Tejada et al. 2009; Bottini et al., 2012). The C3 stage also fits within a long-term warming tendency disclosed by increasing negative $\delta^{18}\text{O}$ values (trend O1 cf. Menegatti et al., 1998; de Gea et al., 2003; Luciani et al., 2006; Ando et al., 2008, Erba et al., 2010; Stein et al., 2011), which begins in Lower Aptian segment C2, in the *Globigerinelloides blowi* biozone (Figures 1–1, 1–2).

- An abrupt stepwise positive shift (segment C4) of the $\delta^{13}\text{C}$ values that culminate with a positive excursion corresponding to segments C5–C7 within the *Leupoldina cabri* foraminiferal biozone. OAE-1 corresponds to carbon isotope segments C4 to C6 (Figure1–1)

Figure 1-2 Stratigraphic position of Oceanic Anoxic Event 1a framework according to Ogg & Ogg (2008) and to this work based on Moreno-Bedmar et al. (2009, 2010, 2012) and Reboulet et al. 2012.

- The interval with the highest $\delta^{13}\text{C}$ values in the Lower Aptian corresponds to segment C7 (the “Cismon Event” *sensu* Menegatti et al., 1998), which extends from the upper part of the *Leupoldina cabri* to the lower part of the *Globigerinelloides ferreolensis* planktonic foraminiferal zone (Menegatti et al. 1998; Bralower et al. 1999; de Gea et al. 2003). The interval correlates with the top of the *Deshayesites weissii* to the lower *Epicheloniceras*

subnodosocostatum ammonite biozones (Figure 1–2). The stage C7 also coincides with a general tendency to increased $\delta^{18}\text{O}$ values that begins in the stage C4 (trend O2 cf. Menegatti et al., 1998; de Gea et al., 2003; Luciani et al., 2006 and Ando et al., 2008; Stein, 2011) interpreted as a long term cooling period.

- An interval of decreasing $\delta^{13}\text{C}$ values labeled segment C8, correlative with the *Globigerinelloides ferreolensis* planktonic foraminiferal zones, and most of the *Epicheloniceras subnodosocostatum* ammonite biozones (Figure 1–2).

In general, the stable carbon isotope segments defined by Menegatti et al (1998), prior to, during, and after OAE-1a, can be identified in sediments from ocean basins and epicontinental shelves, regardless of the differences in amplitude among local $\delta^{13}\text{C}$ curves. These differences may be a result of the effects of local sedimentary rates, diagenetic history, local paleoenvironmental conditions, as well as variance in the source and proportion of the carbonates and organic matter.

Carbon organic-rich levels or black shales characteristic of OAE-1a occur within intervals C3 to C6 in the Cismon section (Figure1–1), but the temporal extent of these black shales may vary at different localities. In addition to OAE-1a, less prominent, and non-correlative younger organic-rich levels have been identified in $\delta^{13}\text{C}$ segments C7 and C8 (Figure 1–2, 1–3) in sediments of the Vocontian Basin (Noire and Fallot levels; Herrle et al. 2004; Herrle et al. 2010), the Gargano Promontory (Luciani et al. 2006), the Basque-Cantabrian region (Millán et al. 2008), and the Prebetic and Subbetic ranges (de Gea et al. 2003; de Gea et al. 2008a). Such younger and not necessarily correlative levels, have been attributed to the *Leupoldina cabri* planktonic foraminiferal zone (Luciani et al., 2006), and to the *Dufrenoya furcate* (Millán et al. 2008).

Figure 1-3 Distribution of the most important organic-rich intervals in the Vocontian Basin, after Herrle et al. (2004)

1.2 Main Hypothesis

Despite variability of the carbon isotope signal observed between shallow, hemipelagic and pelagic settings (Gaona-Narvaez et al., 2013a, see figs. 4–8 and 4–9 herein), the pattern of temporal distribution of the stable carbon isotope values is consistent with well-established biostratigraphic zones; therefore, it can be used as reliable reference for chemostratigraphic correlation within Lower and Upper Aptian series. Hence, it can be hypothesized that the combined use of these sets of data has the potential to help clarify the exact chronostratigraphic position of organic-rich intervals in local basins, as they may not necessarily be related to more widespread anoxic events and global perturbations in the carbon cycle.

Figure 1-4 Location of the Basco-Cantabrian Basin and the Tablazo Magdalena Basin in the paleogeography of the Aptian. Paleogeographic map after Scotese (2011).

1.3 General Objective

In the dissertation I address the issue concerning the differentiation of OAE-1a from other Lower Aptian anoxic episodes. In order to accomplish this objective I chose two sequences from each side of the Tethys Sea, one deposited in neritic environments of the Basco-Cantabrian Region (Spain), and the other in the Eastern Cordillera of the Tablazo-Magdalena Basin,

(Colombia), Figure 1–4. My inquiry also examines the interplay of local contributing factors in the development of organic-carbon-rich deposits in the selected Aptian localities, in order to further our understanding of the processes of carbon sequestration in shallow water environments.

1.4 Methodology Summary

The dissertation is focused on the study of outcrops and samples collected from the lower part of the Madotz Limestone, Madotz Section (Basque Cantabrian Region, Spain; Gaona-Narvaez et al., 2013a, Figure 4–1 herein), and of the interval including the top of the Rosablanca Formation and the lower part of the Paja Fm, at the Curití Quarry (Eastern Cordillera, Colombia; Gaona-Narvaez et al., 2013b, Figure 5–1 herein). My approach includes the integration of stable carbon isotope ($\delta^{13}\text{C}_{\text{org}}$), total organic carbon (TOC) and total inorganic carbon content (TIC), as well as ammonite biochronology in order to determine the age of the studied intervals and their relation to Lower Aptian OAE-1a (~120 Ma). I further integrate microfacies analyses, elemental analyses (major and minor), and biomarker evidence to infer changes in the redox conditions at the water/sediment interface during sedimentation. The origin and thermal maturation of the organic matter in the organic-rich levels is addressed through the study of kerogen and bitumen in the organic matter by using pyrolysis Rock-Eval and biomarker analyses. Finally, the integration of the results of microfacies analyses, TOC, TIC, XRD bulk and clay mineralogy, and elemental analyses helps to infer the role of local factors in the production and preservation of organic-rich rocks at the selected sites, particularly the role of nutrients, terrigenous input and climate.

1.5 Specific Questions

The multiproxy approach aims at answering the following main questions:

- What is the age of C_{-org} rich levels in the study areas?
- Are the Lower Aptian organic-rich levels in the Colombian section related to OAE-1a, or do they correspond to a later anoxic event?

- Is the relative enrichment in organic carbon at the Madotz section related to the development of anoxic/suboxic conditions coupled with an increase in local productivity? Is there a relationship between organic matter preservation and accommodation space during the Aptian in the studied locations?
- What is the origin of the organic matter in the organic-rich levels?

1.6 Organization of the Dissertation

The bulk of the dissertation is organized as chapters representing separate research articles, either published, in press, or submitted that address general and specific questions as stated above.

- Chapter Two provides the background geological information about the basins where the studied sections are located. It also provides a general physical stratigraphy, and lithological descriptions of each section based on both field and thin section observations.
- Chapter Three describes in detail the specific methods and materials used for data acquisition.
- Chapter Four was published as an article (Gaona-Narvaez et al., 2013a). This chapter presents total organic and inorganic carbon, stable carbon isotope data of 62.5m of the Madotz section (Spain). The chapter also integrates and discusses the biostratigraphy and stable carbon stratigraphy that demonstrate the record of OAE-1a in the section. The data of this chapter show that the Madotz section can be correlated with other locations with OAE-1a, but the temporal extent of relatively C-org-rich facies indicative of oxygen depletion during OAE-1a in the outer ramp/platform setting is shorter than reported elsewhere for organic-rich shale facies in pelagic and hemipelagic environments. These results also demonstrate that organic-rich deposits during OAE-1a are heterochronous. The chapter includes a tentative calculation of rates of sediment accumulation (without density correction) for the different stable carbon isotope segments of OAE-1a at Madotz.
- Chapter Five corresponds to a research article accepted as a book chapter, currently in press (Gaona-Narvaez et al., 2013b). This chapter presents and discusses stable carbon isotope

values, total organic and inorganic carbon content, pyrolysis analyses, and ammonite biostratigraphy of 23m of the Curití section (Colombia). The data of this chapter demonstrate that the organic-rich interval recorded at the base of the Paja Fm at the Curití Quarry is Lower Aptian in age, but is younger than OAE-1a and correlates with C-isotope segment C7. This C_{org}-rich level is presumably correlative with the European ammonite biozone *Dufrenoiya furcata*.

- Chapter Six describes and interprets the microfacies of the Madotz section that developed before, during and after OAE-1, as well as changes in the sedimentary paleoenvironments and relative sea level in the studied section. In addition, I present results on elemental analyses (major, minor, trace elements), bulk and clay mineralogy, pyrolysis and biomarkers, in order to support my interpretations of the paleoenvironmental changes associated with OAE-1a, including redox conditions, and paleoclimate. Part of the discussion is also dedicated to the evidence for thermal maturation in the section, and the origin of the organic matter during the peak of dysoxic conditions in the section.

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2 GEOLOGICAL SETTING

The two sites studied were selected for their excellent rock exposures and accessibility:

1) Madotz section (Basco-Cantabrian Region, Spain); 2) Curití Quarry (Eastern Cordillera, Colombia).

2.1 Madotz Section (Basque-Cantabrian Region, Navarra, Spain)

The Madotz section is located immediately northwest of the town of Madtoz (Navarra, sheet #114 Alsasua 1:50000: lat. 42°56'24" N, long. 1°52'30" W), at the limit between the provinces of Guipuzcoa and Navarra (Spain), Fig. 2–1. The section is on the southeastern portion of the “Sierra de Aralar”, a western extension of the E-W trending Spanish Basque Pyrenees.

The geologic history of the Aralar Mountains is directly related to the tectonic evolution of the Basque-Cantabrian region, which developed from a Mesozoic extensional/transtensional regime, to a compressional system in the Paleocene during the collision of the Iberian and European plates (García-Mondejar et al., 1996b; Rosales et al., 2002). The Basque-Cantabrian region was part of an intracratonic to pericratonic basin that developed as a result of four major Mesozoic rifting phases (Early Triassic, Late Triassic, Middle-Late Jurassic, and Early Cretaceous), during the opening of the North Atlantic Ocean and the Bay of Biscay. Aptian and Albian carbonate and terrigenous successions constitute important well-exposed sequences in the Sierra de Aralar, where they may reach up to 5000 m at certain locations. These sequences were affected by synsedimentary tectonism, and their sedimentation coincides with the time of transition from rifting to spreading in the adjacent Bay of Biscay (García-Mondejar et al., 1996a; García-Mondejar et al., 1996b). The structural pattern observed in the Aptian and Albian of the Basque-Cantabrian region is attributed to a transtensional regime, which led to NW-SE sinistral strike-slip faults distinctly concentrated in the Bilbao and Gernika area (Fig. 2–2). This area behaved as depocenter where the main siliciclastic systems came together (Fig 2–2).

Figure 2-1 Geographic location of the Madoz section within the Basque-Cantabrian region, Spain.

Figure 2-2 Aptian-Albian geological structures of the Basque-Cantabrian, after García-Mondejar et al., 1996b.

2.2 Mesozoic Stratigraphic Framework of the “Sierra de Aralar”

The main Jurassic and Cretaceous units in the stratigraphic succession of the Sierra de Aralar (cf. Duvernois et al., 1972) illustrate the overall variability in the sedimentologic evolution of the study area. These units are as follows:

- Lower and middle Jurassic coastal and open marine carbonate rocks (oolitic limestones, micrites and biomicrites rich in ammonites).
- Upper Jurassic shallow marine sandy carbonates (bio-, oo- and pelsparites, as well as dolomites) and silicified reefal carbonates.
- Uppermost Jurassic to Barremian limestones (micrites, microsparite or biomicrites bearing charophytes, ostracods or mollusks), claystones, sandy claystones and sandstones

deposited in freshwater and brackish to shallow marine environments. These units are considered the local equivalent of Puberckian and Weldian series.

- Widespread Barremian marine unit of organic-rich limestones and shales with *Astarte* that predate the Aptian transgressive deposits at the Sierra de Aralar. Predominantly terrigenous marine deposits continue into the Lower Aptian (Bedoulian).
- Aptian and Albian rudistid-bearing carbonates (Urgonian facies) deposited on wide carbonate platforms separated by intervals dominated by terrigenous components (orbitolinid-rich marlstones and mudstones). The Aptian and Albian carbonate and terrigenous rocks constitute the so called “Urgonian complex” (Duvernois et al., 1972), which is divided in six stratigraphic/mapping units (Duvernois et al., 1972; see figs. 2–1) that crop out in the study area.

2.3 Lithostratigraphy of the Lower Aptian Succession at Madotz

The target of the dissertation is the lower part of the Aptian succession outcropping at Madotz, which includes the basal calcareous unit of the “Urgonian complex” of the Sierra de Aralar (figs. 2–1, 2–3-2–5).

Detailed macroscopic and microscopic analyses, and paleoenvironmental interpretation of the 62.5 m section (figs. 2–4, 2–5) studied at Madotz are provided in chapters 4 and 6. Thus, the present chapter provides a succinct overview of the outcrop and microfacies.

From the lowest visible part of the outcrop at Madotz, the Aptian of the section (Fig. 2–3) includes a predominately siliciclastic Unit 1 (*sensu* Cherchi & Schroeder, 1998, or “argiles schistosées jaunâtres” of Duvernois et al., 1972), overlain by Unit 2, or “Madotz limestone” including subunit 2a (coral-algae-bivalve-rich limestone), subunit 2b (orbitolinid-rich marls and limestones), and subunit 2c (rudistid- rich limestone). This terminology of Unit 2 was used by Cherchi & Schroeder (1998), and is equivalent to “Ensemble II” in Duvernois et al., (1972). Subsequent authors (García-Mondejar et al., 2009; Millán et al, 2009; Millán et al., 2011) tried to

formalize these units into formations and placed units 1, Subunits 2a and 2b in the Errenaga Formation, whereas Subunit 2c was included in the Sarastarri Formation. My dissertation uses the informal stratigraphic units proposed by Duvernois et al. (1972) because they are supported by detailed regional mapping (Fig. 2–1), and consistent biostratigraphic data.

Figure 2-3 View of the study area at Madotz. Units 2a, 2b and 2c correspond to the subdivisions of the Madotz Limestone (Satellite image and landmarks after Google Earth).

The lowermost three meters of the section, or Unit 1, consists of bioturbated, medium gray to olive gray (N5, 5Y 4/1) claystones. At the field scale the fossil association reveals rare shells, either whole or fragmented, of endobenthic bivalves (tellinoids, nuculoids, arcoids), gastropods (Aporrhaidae), ammonites, decapods, wood fragments, and burrows 3–5 mm in diameter (bioturbation index: 3).

The superjacent subunit 2a of the “Madoz Limestone” (“Avant-barre de Madoz” cf. Duvernois et al., 1972) is 20 m thick. The basal 2.5 m of the unit (3 m to 5.6 m from the base of the section) is transitional from the terrigenous facies to predominately carbonate Urgonian facies. The transitional interval consists of 20–30 cm-thick tabular interbeds of medium dark gray

(N4) biocalcarenites with bivalves, gastropods, *Pseudocyclammina hedbergi*, *Choffatella decipiens*, *Marssonella* sp., and textularids; dark gray (N3) packed biocalcarenite (micritic matrix) with corals and bivalves; and olive gray (5Y 4/1), sparse biomicrudite with common bivalves, *Palorbitolina lenticularis*, and textularids.

The upper part of subunit 2a is 17.4 m thick (Fig.2–4) and consists of medium light gray (N6), light olive gray (5Y 6/1), and yellowish gray (5Y 8/1) nodular, packed and sparse biocalcarenite and biocalcirudites with mostly wavy-bedding (10–170 cm-thick). Microscopically they are highly recrystallized biomicrites and biomicrudites with rounded, moderately to poorly sorted fragments of corals, non-rudistid bivalves, echinoderms, sponges, calcareous algae (*Boueina*), bryozoans, and scarce rudistids. At the level between 16.6 and 18 m the biocalcarenites correspond to a moderately sorted peloidal biomicrites. Other coarse components consist of coated grains, aggregate grains, and skeletal material showing packed fabric. Abundant articulated bivalves, corals echinoids, and minor orbitolinids (dominantly the conical morphotype), calcareous algae (udoteacean and corallinean), lituolid and miliolid foraminifera constitute most of the fossil assemblages.

Subunit 2b is 24.4 m thick (from 23 to 47.4 m), but the basal interval from 23 to 26.6 m of was buried under slope wash. The visible part from 26.6 to 42.3 m (figs. 2–4, 2–5), comprises 15–210 cm-thick interbeds of indurated marly limestones (biocalcirudites and biocalcilutites), bioclastic marlstones, and less indurated marlstones, claystones and shales. The Indurated beds are medium dark gray (N4), olive gray (5Y 4/1), medium dark gray (N4) and dark gray (N3) in color; they are characteristically bioturbated, and in most of the beds display wavy primary structures. These beds are sparse-to-packed biomicrudites and biopelmicrites, fossiliferous micrites and pelmicrites. Complete fossil assemblages include whole specimens and angular fragments of variable amounts of echinoderms, bivalves and benthic foraminifera such as *Palorbitolina lenticularis* (discoidal morphotype), *Choffatella decipiens*,

Figure 2-4 Lithology, and levels of samples collected at the Madotz section. Lithology: packstone (P), wackestone (W), mudstone (M).

Figure 2-5 Panoramic view of the Madotz section. Lithostratigraphic units after Duvernois et al. (1972). The pictures show the location of the most conspicuous shale in the section (1.8 m-thick), as well as the distribution of the beds with orbitolinids (biomcrudites: *Orb bcr*) in the upper part of Unit 2b.

Pseudocyclammina hedbergi and textularids, as well as less common *Marssonella* sp., and *Lenticulina* sp. Less indurated planar beds of bioturbated medium dark gray and dark gray (N4, N3) marlstones and calcareous claystones/silty claystones with similar fossil are intercalated with these layers. Occasional medium and thick planar beds of dark gray to grayish black (N3, N2) calcareous claystones, claystones and clay-shales with dispersive framboidal and nodular pyrite, may show low to no apparent bioturbation. Benthic foraminifera vary from very rare to absent, and echinoderm fragments, calcispheres and ostracods are rare to common.

The uppermost part of subunit 2b (43.3 m to 47.4 m, figs. 2–4, 2–5) comprises medium gray (N5) and medium dark gray (N4) marlstone bedsets, 60 to 180 cm thick, with wavy contacts. Microscopically they consist of grain-supported to matrix-supported, poorly sorted biomicrudites, biomicrites and pelbiomicrites. Allochems include abundant rounded fossil fragments and cortoids. *Palorbitolina lenticularis* (conical and discoidal) dominate the foraminiferal assemblages as found in the lower part of subunit 2b. These beds also contain scattered fragments of non rudist bivalves, brachiopods and echinoderms.

Subunit 2c forms a prominent ledge known as Madotz bar (“Barre de Madoz” cf. Duvernois et al., 1972). The lowest part (47.4–52.9 m) consists of medium gray (N5) and medium dark gray (N4) limestones in 15 to 80 cm-thick parallel wavy beds, with locally large-scale cross bedding. Microscopically, they are essentially poorly sorted, packed biopelmicrites and biopelmicrudites. Fossil assemblages include abundant and diverse benthic foraminifera such as miliolids, lituolids and textularids, as well as common echinoderms, non-rudist bivalves, and corals. Orbitolinids are common only at the base of the interval.

The terminal interval of the section studied (52.9–62.5 m) remains in the lower part of an extensive subunit 2c (*sensu* Duvernois et al., 1972). The interval studied shows characteristically 10 to 40 cm-thick, medium light gray (N6) and light olive gray (5Y 6/1) fine to medium biocalcirudite beds with wavy contacts. Microscopically they consist of poorly sorted, sparse

biomicrudites and packed biopelmicrudites devoid of terrigenous components. The biopelmicrudites include common benthic foraminifers (especially miliolids), fragments of non-rudistid bivalves, rare bryozoans, brachiopods, calcareous algae (*Boueina* sp.), and echinoderms. They intergrade upward into a 2-m-thick massive bed of sparse calcirudite (floatstone), with rudists (requieniids). Requienid-rich facies are found for approximately 85 m more above the studied section (Cherchi and Schroeder, 1998).

Figure 2-6 Biostratigraphy and lithostratigraphy of the Aptian and Albian Section at Madotz according to Duvernois et al., (1972) and Cherchi & Schroeder (1998) compared to the new findings in this work.

2.4 Biochronology of the Madotz section

A comprehensive discussion of the Biostratigraphy of the Madotz section is presented in Chapter 4. The lower part of the section (Unit 1, subunits 2a, and 2b) was initially correlated with the Lower Aptian based on benthic foraminifera taxa of the *Palorbitolina lenticularis* Zone, and presumably the presence of *Deshayesites* cf. *deshayesi* in Unit 1 (Duvernois et al., 1972; Cherchi & Schroeder, 1998), Fig. 2.6, which indicated a biochronologic level correlative with the upper part of the Lower Aptian. Subunit 2c was assigned to the *Orbitolinopsis simplex* Zone (Cherchi & Schroeder, 1998), correlating with the Upper Aptian (Gargasian). In Chapter 4, the chemostratigraphic results coupled with new ammonite taxa collected from Unit 1, and the middle part of subunit 2b support a stratigraphic position corresponding with at least the upper part of the *D. forbesi* Zone (formerly *D. weissii* Zone). The new data thus imply a lower stratigraphic position in the Lower Aptian (Bedoulian) than previously assigned to the section.

2.5 Curití Section (Eastern Cordillera, Colombia)

The Curití section is an active quarry (Cementos Argos Quarry, lat. 6°36'58" N, long. 73°4'32" W) near the town of Curití (Santander), in the Colombian Eastern Cordillera (Fig. 2–7). The study focuses on the uppermost part of the Rosablanca Fm (Barremian age) and the lowermost deposits of the Lower Aptian Paja Fm.

Geologically, the section is located in the former eastern side of the Mesozoic extensional basin, known as the Tablazo-Magdalena basin (TMB, Fig. 2–8), which is interpreted as a rift system oriented NNE-SSW. The basin is limited to the east by a system of horsts in the area of the Santander-Floresta Massif (Etayo-Serna et al., 1976; Fabre, 1987), and to the west by the Palestina Fault in the present area of the Central Cordillera. The TMB was one of the several extensional basins that developed in northwest South America whose formation is still a matter of controversy, whether it is related to the break-up of Pangea or to back-arc rifting behind a subduction zone (Sarmiento, 2001; Rolón, 2004) remains to be clarified.

Figure 2-7 Geographic location of the Curití section. Geological structures in the Eastern Cordillera after Gómez et al., 2007.

The onset of the TMB was related to two initial stretching events between the latest Triassic and the mid-Jurassic; syn-rift deposits of this early stage are represented by the fluvial and lacustrine deposits of Jordan, Giron and Los Santos, Tambor and Arcabuco Formations. Flooding episodes in a N-NE direction lead to diachronous accumulation of evaporites, carbonates and siliciclastic in marginal, littoral and shelf environments between the Berriasian and the Early Aptian; these deposits in different areas of the basin include the Cumbre, Rosablanca, Ritoque, Paja and Tablazo/San Gil Inferior Formations (Etayo-Serna et al., 1976; Etayo-Serna et al., 2003; Allen et al., 1988; Sarmiento, 2001, Rolón, 2004). Three depositional sequences (Latest Jurassic to Late Hauterivian, Early Barremian to Early Aptian, Mid to Late Aptian) have been recognized in the syn-rift succession, with maximal sea levels in the early Late

Valanginian, Early to Middle Barremian, and Late Aptian (Rolón & Carrero, 1996). Tectonic subsidence controlled the basin at least until the Early Aptian, whereas eustatic sea level changes controlled most of the Mid- and Late Cretaceous sedimentation (Sarmiento, 2001; Rolón, 2004). During the Maastrichtian the Mesozoic extensional basin developed into an initial retroarc foreland basin that has evolved into the Middle Magdalena Valley and the Eastern Cordillera since the mid-Eocene (Sarmiento, 2001; Rolón, 2004; Gómez et al., 2005; Barrero et al., 2007).

Figure 2-8 Hauterivian-Barremian facies distribution in the Colombian Andes. Map after Sarmiento (2001).

The Curití section accumulated under conditions of slow subsidence, and a more detailed geologic evolution of the area is discussed in Chapter 5 Carbonate accumulation in the Curití area, locally called Rosablanca Fm, persisted until the Barremian, whereas more distal areas of the basin (Patarroyo, 2004) accumulated black shales (Paja Fm), which became prevalent basin-wide in the Aptian.

2.6 Lithostratigraphy of the Studied Section at Curití Quarry (Eastern Cordillera, Colombia)

The section studied at Curití (Figures 2–9, 2–12) is discussed in details in Chapter 5. Here I present a summary of the 23.3-m that constitute the object of the dissertation.

Figure 2-9 Overview of the sequence studied at the Curití Quarry. The studied 23.3m interval includes the top of the Rosablanca Fm (1.56m) and part of the Paja Formation.

The top 1.56 meters of the Rosablanca Fm ends with a 17cm conspicuous phosphatic bed (Fig. 2–10A, 2–11) defining the boundary with the superjacent Paja Fm. The 21.8 m of the Paja Fm studied consist of black shales and marlstones of the lowest units of the formation at Curití (Figs. 2–9, 2–10B). The most striking feature of the Rosablanca Fm (Figs. 2–10, 2–12) at the section is the rapid lithological change within the 1.56-m interval studied (Blau, 1993). The sequence changes rapidly from medium dark gray (N3), packed, bivalve-rich biocalcirudites (packstones and wackestones) to grayish black (N2) biomicrites (calcimudstones) with gradual increase in organic matter, and phosphatic components. The 17 cm-thick phosphatic boundary bed is pyritic and shows (Fig. 2–10A, 2–11) an irregular basal contact.

The 21.8-m of the Paja Fm (Figs. 2–9, 2–10B) consists of interbedded organic-rich black clay-shales, calcareous clay-shales, marlstones, and lenticular beds of black, non-fossiliferous, and fossiliferous calcimudstones (see Chapter 3). The sequence includes fifteen levels with concretions. The lowermost part (between 1.56 and 7.87m; Figs. 2–10B, 2–12), consists mostly of non-bioturbated black clay-shales, calcareous clay-shales and marlstones with even laminae

alternating with 7–22cm-thick crystalline limestones with apparent wavy lamination.

Figure 2-10 Outcrops of the top 1.56m of the Rosablanca Fm (A); and (B) 7.9m of the Paja Fm showing a shale and marlstone dominated interval. Numbers indicate bed and sample numbers in the stratigraphic log.

Figure 2-11 Details of the fossil content of the phosphatic boundary bed between Rosablanca and Paja Formations. The phosphatic bed shows an irregular base (A), and contains abundant Ancyloceratid ammonites (B, C) and lucinid bivalves (D).

Figure 2-12 Lithology and levels of samples collected at the Curití Quarry Section. Lithology: packstone (P), wackestone (W), mudstone (M).

Fig. 2-12 Continued

Occasional interbeds of black non-bioturbated limestones (4–40cm thick) also occur in the interval. Microscopically, most of all the beds contain rare fossils (up to 10% in certain levels) such as calcispheres, fish bones and scales, ostracods, planktonic foraminifers, and bivalve together with echinoderm fragments at certain levels. Dolomitic crystals may develop around the calcareous fossils. Disseminated framboidal pyrite is present in the matrix, or within fossils. Centimeter- to decimeter- sized concretions occur in this lower part and consist of calcilutites (pelmicrites) with abundant crustacean fecal pellets, rare ostracods, benthic foraminifera, fish bones, and rare ammonite fragments.

The succeeding interval (7.87 to 16.5 m; Figs. 2–10B, 2–12), comprises high-frequency, interbedded, black (N1) calcareous clay shales and marlstones, varying from 12–80 cm thick, to 7–52 cm thick. It also includes tabular, lenticular and concretion-shaped marlstones with fossil contents similar to the adjacent beds. Several levels of fossiliferous marlstones appear with relatively abundant, poorly sorted phosphatized faunas and intraclasts.

The penultimate interval (16.5 to 21 m; Fig.2–12) is composed of interbedded black (N1) marlstones and calcareous shales, with tabular and lenticular calcilutites. These beds are poor in fossils (fish bones, small inoceramids, and calcispheres). The relative abundance of fossils increases within the marlstones at discrete thin levels of muddy biocalcarenites with wavy internal structure, and common shallow-water bivalves (e.g., ostreids). The marlstones contain levels of biocalcirudites (wackestones) concretion that contain mostly bivalves, as well as rare ammonites and gastropods.

The topmost interval studied (21 to 23.35 m) of the section (Fig. 2–12), is more clay rich as the calcilutite interbeds disappear and the sequence is dominated by 5–18cm-thick homogenous marlstones, interbedded with less indurated clayish beds, as well as levels of decimeter-size micritic concretions. The weathered surfaces of these beds appear grayish-brown (Fig. 2–9), and at the field scale observation this interval contain less than 10% fossils, consisting

of phosphatic fish fragments, fewer ammonite fragments, and inoceramid bivalves.

2.7 Biostratigraphy and Biochronology of the Curití Section

The biostratigraphic framework generally applied to delineate the Barremian and Aptian stages in the Eastern Cordillera is focused on ammonites; however, the Barremian-Aptian transition and the Lower Aptian remain unresolved because of a scarcity of specimens related to shallowing of the facies, and the taxa present are stratigraphically not well constrained. The problem is further aggravated by the fact that some index taxa are diachronous, thus making it difficult to establish reliable correlation with Mediterranean ammonite biozones (further discussed in Chapter 5). On the basis of the quality of collected ammonite specimens, and the methods used in their study of Colombian assemblages, the most extensive and reliable zonations established for the region are those proposed by Bürlg (1956) and Patarroyo, (2004) for the Barremian, and Etayo-Serna (1979) for the middle and Upper Aptian (Figure 2–13). Thus, the ammonite biozonation used in this dissertation follows these biochronological interpretations (Chapter 5, Gaona-Narvaez et al., 2013).

Middle Barremian to lowest Aptian ammonites of the genera *Pulchellia*, *Gerhardtia*, *Toxancycloceras*, *Karsteniceras* and *Prodeshayesites* (?) appear in a reworked and phosphatized ammonite assemblage at the boundary between the Rosablanca Fm and the Paja Fm, but the base of the middle Aptian is clearly identified at 16.9 m by the presence of *Riedelites obliquum* and *Epicheloniceras* sp. (*Dufrenoyia sanctorum*-*Stoyanowiceras treffryanus* Zone of Etayo-Serna, 1979). Moreover, an Early Aptian position for the basal segment of the Paja Fm studied at Curití is confirmed by samples collected between 1.9 and 4.8 m, which contain calcareous nannofossil assemblages corresponding to the subzone NC6A. Nannofossil assemblages corresponding to the Lower Aptian subzone NC6B occur in samples between 11.2 and 13.75 m. The base of the calcareous nannoplankton subzone NC7A, transitional between the Lower and middle Aptian was recognized at 16.1 m in agreement with the ammonite biochronology for the area.

Biostratigraphic results on the calcareous nannoplankton were recently acquired, therefore are not included in Chapter 5; they are available in the supplementary information section.

Chrono and magnetostratigraphy (Ogg and Ogg, 2008)			Tethyan ammonites (Ogg and Ogg, 2006; Reboulet et al., 2011)	Ammonite Biozones		
				Burlig, 1956	Patarroyo, 2004	Etayo-Serna, 1979
110	Albian	Early	<i>Douvillericeras mamillatum</i>	Not zoned	Not zoned	<i>Douvillericeras solitae-Neodeshayesites colombianus</i>
			<i>Leymeriella tardefurcata</i>			<i>Parahoplites? hubachi-Acanthohoplites? leptoceratiforme</i>
			<i>Hypacanthoplites jacobi</i>			
	Aptian	Late	<i>Nolaniceras nolani</i>			
115			<i>Parahoplites melchioris</i>			?
			<i>Epicheloniceras martini</i>			<i>Stoyanowiceras treffryanus-Dufrenoyia sanctorum</i>
		Middle	<i>Dufrenoyia furcata</i>			?
			<i>Deshayesites deshaysi</i>			
			<i>Deshayesites forbesi</i>			
			<i>Deshayesites ogilensis</i>			
			<i>Pseudocrioceras waagenoides</i>			
			<i>Colchidites sarasini</i>			
			<i>Imerites giraudi</i>			
			<i>Hemihoplites feraudianus</i>			
			<i>Gerhardtia sartousi</i>			
	Barremian	Late	<i>Ancyloceras vandenheckii</i>	Upper	None or few pulchellids	<i>Colchidites breistroffeni</i>
			<i>Coronites darsi</i>			
			<i>Koelischella compressissima</i>			
			<i>Nicklesia pulchella</i>			
		Early	<i>Nicklesia nicklesi</i>	Lower	Upper: Subzone with <i>Nicklesia</i> , <i>Repletesia</i> , <i>Sempulchella</i> Lower: Subzone with <i>Nicklesia</i>	<i>Nicklesia pulchella</i> <i>Pulchella galeata</i> <i>Pulchella</i> <i>Pulchella</i>
			<i>Spitidiscus hugii</i>			
125						
120						
115						
110						

Figure 2-13 Biostratigraphic zonations applied in the Barremian and Aptian of the Eastern Cordillera in Colombia.

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3 METHODS AND MATERIALS

The current study was accomplished in three main phases:

- 1) Literature review and field geology, in order to select suitable Lower Aptian outcrops that potentially include Oceanic Anoxic Event 1a (OAE-1a), and perform descriptions on the outcrop's physical stratigraphy and lithology. Once the site was selected the study involved systematic sampling for further laboratory analyses.
- 2) Analyses of samples in the laboratory, including microscopic descriptions; evaluation of inorganic and organic carbon content (TIC, TOC), stable carbon isotopes on organic and inorganic fraction ($\delta^{13}\text{C}_{\text{org}}$); elemental analyses by LA-ICP-MS; biomarker analyses by GS and GC-MS, mineralogical analyses by XRD.
- 3) Integration of data, including interpretation of the field and laboratory datasets for paleoenvironmental interpretation, discussion of biostratigraphic data, chemostratigraphic interpretation and correlation with other published locations in the literature; and, preparation and submission of manuscripts to scientific journals.

3.1 Selection of Study Locations, Sampling and Physical Stratigraphy

The selected study site in Spain is located in the immediate vicinity northwest of the town of Madotz (long. 42°56'24", lat. 1°52'30", see Figs. 2-1, 2-3), in the southeastern portion of the "Sierra de Aralar", Navarra. The site was preliminarily described by F. Maurrasse (FIU) and M. Lamolda (University of Granada, Spain) in 2006, and I carried out the first sampling program and description of the section in 2008 (T. Gaona; F. Maurrasse, and J.A. Moreno-Bedmar, University of Barcelona). The lower 62.5 meters of the Madotz section were selected for the study because they include a thick interval of easily accessible Aptian outcrop previously described as units 2a, 2b, and basal part of 2c coined the "Madotz limestone" (Duvernois et al., 1972; Cherchi & Schroeder, 1998), which presumably includes the desired interval for the research project.

Similarly, a preliminary visit to Colombia was initiated in 2007 and the site was chosen after literature review and discussions with staff geologist of the Colombian Geological Survey (Bogota). The Colombian site was also chosen based on level of exposure, accessibility, availability of previous biostratigraphic studies, and presence of organic-rich facies potentially correlative with OAE-1a. The first site selected was nearby the town of Curití Santander, was being analyzed for ammonite biochronology by F. Etayo-Serna (Colombian Geological Survey). The location corresponds to a quarry owned by “Cementos Argos” (lat. 6°36'58" N, long. 73°4'32" W) where limestones of the Rosablanca Formation are exploited uncovering the basal interval of the organic-rich lithologies of the Paja Fm. The interval selected for the study comprises 23.3m of middle Barremian (1.56 m of Rosablanca Formation) to Upper Aptian (21.8 m Paja Formation) exposed along the quarry face (Figs. 2–9, 2–10).

Samples were taken every 10–20 cm intervals in dark hypothetically organic-rich lithologies, and each 30–200 cm in light hypothetically organic poor intervals.

Thickness of inclined beds was measured with a Jacob's staff and a Brunton compass. Field descriptions included bed geometry, nature of the bed contacts, sedimentary structures, color in fresh hand sample, lithology, texture, and fabric for levels thicker than one decimeter. In addition, bioturbation, type, abundance, and preservation of fossils, as well as sorting and packing for coarse bioclasts (>2 mm), were also described.

Numerical values for thicknesses of beds and laminae followed Boggs (2006) and other references herein. Descriptive terms used for the configuration of bedding surfaces are those of Campbell (1967), and color description followed standard color tables of the Geological Society of America (1995).

The nomenclature for field lithological descriptions followed Folk's scheme (1962, 1980), with an integrated version of Durham's scheme (1962) modified by Wright (1992). The nomenclature recommended by Potter et al. (2005) was used for fine-grained rocks,

distinguishing between lithified non-fissile rocks (mudrock, claystone, siltstone), and lithified fissile/laminated rocks (shale, clay-shale, silt-shale). In the study sections, the rocks represented various mixes between carbonate and terrigenous end members, and for this reason initial field classification was later modified using objective values according to the true carbonate content obtained by carbon analyses. Thus, description and graphic representation in the stratigraphic logs use the terms limestone, marlstone, calcareous mudrocks and mudrocks on the basis of the following relative percentages of total carbonate (measured CaCO_3) as follows: mudrock/shale: 0–10% CaCO_3 ; calcareous mudrock/shale: 10–30% CaCO_3 ; marlstone: 30–60% CaCO_3 ; limestone: >60% CaCO_3).

3.2 Microfacies Description and Analyses

Petrographic and microfacies analyses assess the relative composition, depositional environment, and diagenetic processes represented by the samples. Microscopic analyses included observations through conventional transmitted light microscopy assessing the following features: small scale sedimentary structures, rock's framework and texture, composition and relative abundance of different components (grain, matrix, cement); type, preservation, and abundance of allochems; degree of bioturbation, preliminary identification of early diagenetic minerals specially those indicative of redox conditions. The degree of bioturbation of the samples was described according to Bottjer & Droser (1986).

The terms silty, muddy, clayey, sandy, and calcareous, are applied for volumes higher than 10% of silt, mud, clay, sand and carbonate, respectively. The terms pyritiferous/pyritic, ferruginous, phosphatic are applied for volumes between 1–5% of pyrite, iron oxydes, and phosphates, respectively.

Description and identification of carbonate components, textures, fabrics, cements, and minerals in thin sections followed the works of Adams et al. (1984), Scholle & Ulmer-Scholle (2003) and Flügel (2004). Especially useful were the references provided by Flügel (2004) on

studies of Cretaceous platforms. Limited attempts for identifying the benthic foraminifera in thin sections were made using the literature on Aptian carbonate platforms.

Bioclast abundance was assessed in several ways in the thin sections: 1) by comparison with visual estimation charts (Baccelle & Bosellini, 1965) at magnification 20X; by 2) by identifying, counting and determining relative percentages of all identifiable bioclasts on five random fields of view at 20X. Abundance of fine sand and silt quartz grains, and pyrite was obtained by visual estimation using Baccelle & Bosellini's charts (1965) at magnification 20X.

Interpretation of the microfacies was made by comparison with the microfacies models published in the literature.

3.3 Scanning Electron Microscopy with Energy-dispersive X-ray Spectroscopy

Scanning electron microscopy (SEM) depends on the interaction of an electron beam with a sample's surface. When the electrons strike the sample, different signals are generated, and it is the detection of specific signals that produce surface (image) and elemental information on the sample. The signals which provide the greatest amount of information in SEM/EDS are the secondary electrons (surface signal), backscattered electrons (compositional meaning signal), and X-rays (compositional meaning signal).

The SEM analyses were conducted on selected samples with the JEOL JSM 5910LV equipped with an EDAX EDS-UTW detector, available at FIU's Florida Center for analytical Electron Microscopy (FCAEM). The purpose was to obtain more compositional details about the mineral phases present in the silt and clay fraction, presence of early diagenetic minerals indicative of redox conditions, as well as the imaging of those phases, and microfossils. Thin section and rock chips were observed uncoated on low vacuum mode; some samples however were carbon coated for improving the quality of the images.

3.4 Paleontological Preparation and Biostratigraphy

Selected paleontological samples were sent to different specialists, and the integrated results provided a local/regional biostratigraphic framework. Ammonites from Madotz were prepared and analyzed by Dr. Josep Moreno-Bedmar (University of Barcelona), and specimens from Colombia were studied by Dr. Fernando Etayo-Serna (Colombian Geological Survey, Bogota). In addition to ammonite taxa collected *in situ* in the field, other specimens previously collected in the Curití section by the Colombian Geological Survey were also included in the study. All specimens obtained in Colombia were prepared by staff technicians of the paleontological laboratory at the Colombian Geological Survey, and subsequently were deposited at the José Royo y Gómez Paleontological Museum in Bogota.

Smear slides from the Curití section were prepared by T. Gaona to test for presence of calcareous nannofossils, which were sent for identification by Dr. Mihaela Melinte at the Geomar Institute of Sciences in Bucharest, Romania. Smear slides were prepared using scraps of material from fresh rock samples following the method recommended by the U.S. Geological Survey (U.S. Geological Survey, 2013). The nannofossils provided an independent evidence on the age of the Paja Fm. Results of these analyses were not included in any publications (Chapter 5, herein) but are available in the supplementary information chapter.

Both at Madotz and at Curití, planktonic foraminifera were either absent in thin sections or extremely affected by diagenetic growth of dolomite crystals; samples were not disaggregated in search of such microfossils. Samples from Colombia were prepared for palynological analyses by members of the laboratory of Carlos Jaramillo at the Smithsonian Tropical Research Institute, Panama, but the results were unsuccessful because of the high degree of thermal maturity of the organic matter in the studied samples.

3.5 Total Organic Carbon (TOC) and Total Inorganic Carbon (TIC) Analyses

Since anoxic conditions enhance the preservation of organic matter, total organic carbon (TOC) and total inorganic carbon (TIC) analyses provide useful information concerning such environments. The TIC and TOC analyses were performed on all samples using a LECO CR-412 carbon analyzer. The analytical method is presented in detail in Chapters 4 and 5, herein.

3.6 Stable Carbon Isotope Ratios on Organic Matter

The application of stable carbon isotopes in paleoenvironmental reconstruction stems from the processes of photosynthetic uptake of the two main stable isotopes ^{12}C and ^{13}C . Photosynthetic fixation of Carbon involves a very large negative fractionation, therefore organically derived carbon compounds are isotopically light, or they are depleted in ^{13}C relative to the existing $^{12}\text{C}/^{13}\text{C}$ ratio in the atmosphere. Increased productivity coupled with a high rate of sedimentation leads to rapid burial of organic matter thus allowing organic carbon sequestration in the sediment. The process entraps ^{12}C carbon from the system and the water becomes progressively enriched in ^{13}C . Autotrophs will then intake $^{13}\text{CO}_2$ in greater amounts given that the heavier molecule is now more abundant. Therefore, high-productivity events, and periods of organic carbon sequestration, will be recorded in the isotopic composition of organic matter as positive excursions of the $\delta^{13}\text{C}_{\text{org}}$ curve. On the basis of this premise, it is expected that OAE's can be confirmed by a peak of an appropriate positive excursion of the $\delta^{13}\text{C}$ curve (Jenkyns, 1980, among others), given that conditions for the onset of OAE's are coupled with increased carbon sequestration in the sediment. Thus, ($\delta^{13}\text{C}_{\text{org}}$) were performed to determine the positive excursion associated with OAE-1a.

Isotopic measurement on organic carbon was performed at the isotope facility of the Southeast Environmental Research Center (SERC) of Florida International University, and Carrie Rebenack and John Harris were in charge of analytical work. The analytical procedures to determine the isotopic ratios are discussed in Chapters 4, and 5, herein.

3.7 Pyrolysis

Rock Eval pyrolysis is used to measure the quantity, quality, and thermal maturity of organic matter in rock samples, and to assess petroleum potential in sediments. The organic matter in the sample is in the form of Kerogen, complex, high-molecular-weight, disseminated organic compounds in sediments, which are insoluble in non-polar organic solvents, and in non-oxidizing mineral acids (Whelan & Thomson-Rizer, 1993; Killops & Killops, 2005; Peters et al., 2005). The technique is also commonly used to typify the kerogen according to their origin, but it may lose its effectiveness depending of the degree of thermal maturation of the samples, degree of bioturbation of the sediment, degree of mixture between two or more kerogen types, and artifacts created during pyrolysis of the sample. Such artifacts include catalytic effect in samples with smectite and illite-rich matrix, pyrolysis of CaCO_3 in carbonate-rich samples, and hydrocarbon retention in mineral grains (Whelan and Thompson-Rizer, 1993; Dembicki, 2009). Pyrolysis on total rock samples was performed on seven samples representative of all fine-grained lithologic types present in subunit 2b from Madotz (Spain), as well as 7 samples collected from the top of the Rosablanca Fm to the lower 10m of the Paja Fm, Curití Quarry (Colombia). Analyses were performed at the Center of Petroleum Geochemistry at the University of Houston following the protocol written by Dr. Adri Bissada, using a ROCK-EVAL II-PLUS analyzer (Vinci Technologies). Michael Darrel was in charge of the analytical work. The analytical method consists of a programmed temperature heating (in a pyrolysis oven) in an inert atmosphere (helium) of a small sample. Whole rock samples (50–100 mg) are powdered, weighed accurately into a metal crucibles fitted with a fritted-disk bottom and fritted-disk cap. Each crucible is placed on the auto-sampler tray and is then conveyed sequentially into a furnace initially maintained isothermally at 300°C. Free hydrocarbons are volatilized and quantified by the instrument's flame ionization detector (FID) to give Peak 1 ("S1" in mg hydrocarbons / g rock). The furnace temperature is then automatically increased to 550°C at 25°C per minute. This

is the volatilization phase of the very heavy hydrocarbons compounds ($>C_{40}$), and the cracking of nonvolatile organic matter. Within the temperature range we used, kerogen will crack to give hydrocarbons, measured by the FID to give Peak 2 (“S2” in mg hydrocarbons / g rock), and CO_2 , released in the 300°- 390°C range is measured by a thermal conductivity detector (TCD) within the instrument to give Peak 3 (“S3” in mg CO_2 / g rock). The S2 parameter reaches its maximum at a temperature called T_{max} that depends on the nature and maturity of the kerogen. The temperature at the maximum rate of evolution of cracked volatiles (T_{max}) is measured automatically, but can also be monitored visually. The instrument is calibrated daily using standards both at the beginning of the work period and at regular intervals thereafter. Crucible blanks are run routinely.

The four basic parameters obtained by pyrolysis (Tissot and Welte, 1984) and reported are the following:

- *S1*: The amount of free or distillable hydrocarbons (gas and oil) present in the rock in milligrams/gram rock; i.e., available for migration.
- *S2*: The amount of hydrocarbons generated from kerogen upon pyrolysis of non-volatile organic matter; i.e., residual generation potential (milligrams/ gram rock) of producing hydrocarbons should burial and maturation continue.
- *S1+S2*: The total amount of hydrocarbon generation potential of the rock; i.e., fraction of original generation potential which has been effectively transformed into hydrocarbons in rock (*S1*) + residual generation potential (*S2*).
- *S3*: The total amount of CO_2 generated from kerogen upon pyrolysis (milligrams/gram rock). *S3* indicates the amount of oxygen in the kerogen and is used to calculate the oxygen index.

- *HI*: Hydrogen enrichment index, or simply the Hydrogen Index (milligrams hydrocarbons/gram organic carbon). This is a measure of the hydrocarbon generating potential remaining in the kerogen as opposed to that of the whole rock.
- *OI*: Oxygen enrichment index (milligrams CO₂/gram organic carbon).
- *KTR*: Kerogen transformation ratio (S₁/S₁+S₂), described by IFP (Institut Français du Pétrole) as the “Production Index”; i.e., proportion of already generated hydrocarbons to total quantity of hydrocarbons that could presumably be thermally generated by complete conversion of kerogen. The proportion of the amount of hydrocarbons released in the first stage of heating to the total amount of hydrocarbons released and cracked during pyrolysis is sometimes used as a maturation index, provided the samples are contamination-free.
- *T_{max}*: Pyrolysis temperature with maximum yield of hydrocarbons from kerogen pyrolysis (top of S₂ peak). *T_{max}* values increase with increased geothermal history and indicates the stage of maturation of the organic matter.

3.8 Biomarker Analyses

A biomarker is an organic compound in a geological sample that can be structurally related to its precursor molecule which occurs as a natural product in a living organism or any source material (Peters et al., 2005; Killops & Killops, 2005); therefore they are useful to determine depositional environments and source-related parameters of organic-rich rocks. Biomarkers not only provide information about the origin of the bitumen fraction of the organic matter, but also about its thermal maturation. Bitumen extraction, chromatographic separation of saturated and aromatic compounds, gas chromatography and mass spectrometry (GC, GC-MS), and the identification of the different compounds on chromatograms by matching with a mass spectral library was carried out by Weatherford Laboratories (Shenandoah, TX).

Biomarker identification of rock extracts was conducted on selected samples from the studied locations at the levels displaying the highest TOC's. Fingerprints, saturated and aromatic compounds were analyzed from one sample in Madotz section (subunit 2b, sample ES-08-46b). Fingerprint analyses and saturated biomarkers were identified on four samples from the Paja Formation at Curiti (samples CO-09-07, CO-09-17D-2, CO-11-43, and CO-11-61).

The samples submitted to Weatherford Laboratories were prepared and analyzed according to the following protocol:

In order to obtain the bitumen, about 20–50 g of rock is ground to 60 mesh, weighed, placed in a cellulose Soxhlet thimble, and then extracted with dichloromethane using Soxhlet apparatus. Both the Soxhlet thimble and apparatus are run through the extraction process before the addition of the sample to make sure there is no contamination within the extraction system. Freshly activated copper metal is added to the refluxing solvent at the beginning of the extraction process for the removal of any elemental sulfur that may be extracted along with the bitumen. The extraction is allowed to continue until no additional color is observed leaching from the sample (typically overnight). At this point the extraction is stopped and the extract filtered through a pre-extracted Whatman #40 filter paper. Solvent is then carefully evaporated from the filtrate and the amount of extracted organic matter (EOM) is obtained by transferring it to a pre-weighed sample vial.

Because of potential interferences between some classes of aromatic and saturated biomarkers it is traditional to separate saturated and aromatic compounds such that each fraction can be analyzed individually. Medium pressure liquid chromatography (MPLC) was used to isolate the saturated and aromatic fractions. After separation, rock extract was analyzed for fingerprints with an HP6890 gas chromatograph. Biomarkers were identified on both the saturated and aromatic hydrocarbon fractions using gas chromatography-mass spectrometry (GC-

MS), with an HP6890 gas chromatograph, equipped with an on-column injector, coupled to a HP5973 mass-selective detector (MSD).

The saturated biomarkers were separated using a DB-5 column (60 m * 0.25 mm * 0.25 µm film thickness), and the following temperature program: from 100°C (0 min) to 170° C at 20° C /min, then to 290° C at 1.5° C /min, and finally to 320° C at 2° C /min (hold 20 min). The carrier gas was He at constant flow (0.8 mL/min). The MSD instrument was operated in selected ion monitoring mode (SIM, 0.95 cycles/sec). Ions were collected in two time windows extending from 5 to 30 minutes and from 30 to 118.5 minutes.

The aromatic fraction from the GC-MS was separated in a DB-1 column (60 m * 0.25 mm * 0.1 µm film thickness) using a temperature program from 70° C (3 min) to 150° C at 1.5° C /min, and to 315° C at 3° C /min (hold 20 min). The MSD was operated on selected ion monitoring mode (SIM, 0.98 cycles/sec). The carrier gas was He at constant flow (0.9 mL/min). Ions were collected in two time windows extending from 5 to 77.8 min, and from 77.8 to 131.33 min. For both aromatic and saturated compounds, in all windows the dwell time was set to 20 ms for each ion.

3.9 X-Ray Diffraction of Bulk Mineral and Clays

Clay minerals are the most characteristic component of fine-grained siliciclastic rocks (e.g. kaolinite, illite, smectite, chlorite and sepiolite-palygorskite), and mostly a byproduct of weathering. Clay mineral composition in Mesozoic and Tertiary rocks mainly reflects a combination of climate, relief, and source rocks, although clay particles show differential transport in suspension, differential sensitivity to change of fresh to saline water, and mineralogical modification during burial (Potter et al., 2005). Identification of clay minerals is commonly achieved by X-ray diffraction (XRD) that also provides information about the bulk mineralogy of the fine fraction.

A total of 17 samples were analyzed for bulk mineral and specific clay contents performed at the Illinois Geological Survey (ISGS, Champaign), where the geologist Shane Butler was in charge of the analytical work. Measurements were performed on a Scintag XDS 2000 diffractometer, and the Jade+R software (Materials Data Inc.) was used for semi-quantitative data assessment. In the preparation for bulk-mineral analyses the samples were treated with DI water in a micronizer and centrifuged. Once the supernatant was eliminated, the remaining material was dried, homogenized and, then packed into an end-loading sample holder as a random powder bulk-pack to be analyzed in the diffractometer. Step-scanned data were collected from 2° to $60^{\circ} 2\theta$ with a fixed time of 5 seconds per $0.05^{\circ} 2\theta$ for each sample.

Analyses of samples for XRD clay mineralogy uses oriented slides of clay-sized particles ($<2\ \mu\text{m}$) with sample preparation based on techniques by Moore & Reynolds (1997), and Goetsch et al. (2012). XRD slides were prepared with 20 to 30 g of sample soaked overnight in deionized water in a covered 100-ml beaker. The mixture was stirred and allowed to settle, and one-third of the clear supernatant was removed. The beaker was then refilled with deionized water, and two drops of sodium hexametaphosphate dispersant. After stirring and allowing the mixture to settle for 15 minutes, a portion of the supernatant was pipetted onto a glass slide, dried overnight in order to be analyzed with the diffractometer. Clay mineral content was calculated after two treatments (overnight air drying and treatment with ethylene glycol for 24h), to display the change in spectra by comparing peak height ratios among expandable clays (smectite or mixed layer smectite), illite, kaolinite, and chlorite. Air-dried and glycolated samples were step-scanned from 2° to $34^{\circ} 2\theta$ with a fixed time of 5 seconds per $0.05^{\circ} 2\theta$ for each sample. Estimates were produced in relation to the area based on Moore & Reynolds (1997).

3.10 Elemental Analyses (Major, Minor and Trace Elements)

Bulk chemical composition of mudrocks supply information on the provenance of the terrigenous detrital materials initially produced by interplay of tectonics and climate, and later

transported by fluvial or eolian processes into the basins. Elemental analyses further help assessing the supply of nutrient, and the redox conditions at the water/sediment interface and pore waters in fine-grained sedimentary rocks (Sageman & Lyons, 2004; Brumsack, 2006; Piper & Calvert, 2009).

Nineteen samples from subunit 2b of the “Madotz Limestone” were processed for elemental analysis by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) performed at the Trace Evidence Analysis Facility at Florida International University. LA-ICP-MS is a validated technique that allows the simultaneous determination of major, minor and trace elements on samples of soil and sediment with limits of detection as low as 0.01 mg/kg (Arroyo et al., 2009). The list of identified elements in the analysis includes: Al, Si, Ca, Fe, K, Mg, P, Ti, Mn, V, Cr, Co, Ni, Cu, Zn, A, Mo, Ba, Th, U, and V.

The technique uses pressed sediment pellets spiked with scandium oxide (concentration of 1000 ppm) in 3% acid solution as internal standard. The pellets were ablated in a CETAC LSX-500 with a 200 μ m spot size at 10Hz frequency, and 3.01mJ of energy for 60sec. Four pellet replicates were analyzed for each sample and their average reported. Only values with relative standard deviations below 20% were interpreted. The micro-droplets generated by interaction between the laser and the particles were analyzed in an ELAN-DRCII –ICP-MS (Perkins) using He as a carrier gas. Data were processed with GLITTER software (GEMOC, Macquarie University, Australia), or with GEOPRO software (1999, v 1.0, CETAC, USA). The following standards were used: sediment reference material PACS-2 (National Research Council of Canada); soil reference materials, SRM NIST 2710 (Montana Soil), and NIST 2704 (U.S. Department of Commerce, National Institute of Standards and Technology).

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4 STABLE CARBON ISOTOPE STRATIGRAPHY AND AMMONITE BIOCHRONOLOGY AT MADOTZ (NAVARRA, N SPAIN): IMPLICATIONS FOR THE TIMING AND DURATION OF OXYGEN DEPLETION DURING OAE-1A

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Abstract

Detailed stable carbon isotope, and biostratigraphic data based on ammonites allow us to reinterpret the timing of the different units of Madotz section (62 m-thick; Navarra, N Spain), relative to OAE-1a. We also made inference on bulk sedimentary rates and duration of the intervals that include facies indicative of oxygen depletion.

The lowermost part of the sequence includes the predominately siliciclastic Unit 1 (3m) overlain in ascending order by subunits 2a (20 m), 2b (24.4 m) and 2c (basal 15 m studied) of the “Madotz Limestone”. Subunits 2a and 2c consist of Urgonian type pure carbonate rocks. In contrast, subunit 2b consists of carbonate-siliciclastic-mix facies (24.4 m-thick) including beds of claystone and clay-shale with dispersive pyrite, with scarce or absence of benthic foraminifera suggestive of oxygen-depleted conditions, and intermittent orbitolinid-rich intervals.

$\delta^{13}\text{C}_{\text{org}}$ data within subunit 2b, between 26.6m and 49.2m, shows two excursions of 4.21‰ and 3.34‰, separated by a central segment with more uniform values around -22.56‰. Compared to the high-resolution $\delta^{13}\text{C}$ stratigraphy of the early Aptian of the Alpine Tethys (Menegatti et al., 1998), these two positive excursions correlate with segments C4 and C6 of OAE-1a, whereas the central segment is correlative with segment C5, respectively.

New ammonite findings include *Deshayesites cf. forbesi* Casey, and *Pseudohaploceras?* sp. in the uppermost part of Unit 1, as well as *Deshayesites cf. forbesi* Casey, *Pseudosaynella bicurvata* (Michelin), and *Pseudosaynella raresulcata* (d’Orbigny) in the middle part of subunit 2b. The presence of *Deshayesites cf. forbesi* in unit 1 (0–37.7 m) and subunit 2b (lower 14.7 m), the first appearance datum of *Pseudosaynella* in subunit 2b, and the high relative abundance of

Pseudosaynella specimens, support a stratigraphic position correlative with at least the upper part of the *Deshayesites forbesi* Zone (formerly *Deshayesites weissi* Zone). Such ammonite faunal assemblage implies a lower stratigraphic position in the Lower Aptian (Bedoulian) than previously assigned to the section.

Segments C4 and most of C5, make part of the lower part of subunit 2b and correspond to the upper part of the *Deshayesites forbesi* Zone. Based on chemostratigraphic correlations with published Spanish sections (Barranco de las Calzadas, Cap de Vinyet and Cau) in which calibrations of $\delta^{13}\text{C}_{\text{carb}}$ stages with ammonite zones was possible, we infer that the interval of the Madotz section between 37.7 m and 53.1 m, or the upper part of subunit 2b and the basal part of subunit 2c, whose $\delta^{13}\text{C}_{\text{org}}$ signal is indicative of stages C5, C6, and perhaps the beginning of stage C7, is also correlative to the *Deshayesites forbesi* Zone. Average bulk sedimentary rate for C-isotope stages C4 to C6 of OAE-1a ranges from 1.8 to 2.09 cm/ky in the Madotz section.

Facies indicative of oxygen-deficiency are restricted to C-isotope stage C4 and part of C5 of OAE-1a. Hypoxic conditions lasted about 95.2 to 120 ky and are coeval with deposition of the most prominent claystone and clay- shale layers (1.8 m-thick) which display the lowest TIC values (8.16 to 18.93 weight % CaCO_3) and the highest TOC in the section (0.4–0.97%).

4.1 Introduction

Lower Aptian (~120 Ma) Oceanic Anoxic Event 1a (OAE-1a, Arthur et al., 1990) interpreted as a prominent episode of deep perturbation in the carbon cycle (Menegatti et al., 1998; Ando et al., 2002), reported to have lasted between 1.0 and 1.3 Ma (Li et al., 2008). OAE-1a took place in a global context of intense volcanic activity in the Pacific (Larson, 1991; Sinton and Duncan, 1997; Kerr, 1998; Méhay et al., 2009; Tejada et al., 2009), high oceanic surface water temperatures and reduced equator to poles thermal gradient (Frakes, 1999; Pucéat et al., 2003), generalized high sea level (Haq et al., 1987; Skelton, 2003), and common local episodes of

increased marine primary productivity (Erba and Tremolada, 2004; Dumitrescu and Brassell, 2005; Luciani et al., 2006; de Gea et al., 2008b; Heldt et al., 2008).

OAE-1a coincides with worldwide accumulation of organic-carbon-rich sediments in pelagic and hemipelagic areas (Menegatti et al., 1998; Bellanca et al., 2002; Dumitrescu and Brassell, 2005; Luciani et al., 2006; Rückheim et al., 2006; Heldt et al., 2008), as well as deposit of neritic microbial carbonates in shallow waters of the southeastern Arabian platform of Oman (Pittet et al., 2002; Immenhauser et al., 2005; Rameil et al., 2010) and the Adriatic region (Huck et al., 2010). In contrast, the sedimentological record of rudistid limestone to orbitolinid facies, and phosphatic-rich levels indicates flooding of carbonate platforms in the northern Tethys margin and the Black Sea area at the time of OAE-1a (Wissler et al., 2003; Masse et al., 2009).

Also, the documented paleoenvironmental record of OAE-1a time interval in shallow-water environments indicates that in most locations accumulation took place under fully oxygenated conditions (Immenhauser et al., 2005; Burla et al., 2008; Millán et al., 2009; Embry et al., 2010; Huck et al., 2010; Bover-Arnal et al., 2011; Najarro et al., 2011). However, at that time, short and long-term hypoxic conditions developed not only in outer shelves and platforms (Gaona-Narvaez et al., 2009a), but in shallow intertidal environments as well (Gertsch et al., 2010). Uncertainties still remain concerning the duration, frequency and intensity of these oxygen-depletion episodes in shallow settings, and whether these types of environments have the potential to locally generate organic-rich deposits at the time of OAE-1a.

In the present study of the Madotz section (Sierra de Aralar), Basque-Cantabrian Region, Spain, we use a multi-proxy approach that includes the integration of new data set of total inorganic carbon (TIC, weight % CaCO_3), total organic carbon (TOC, weight % C), stable carbon isotope ($\delta^{13}\text{C}_{\text{org}}$), and ammonite biochronology in order to assess the presence of OAE-1a in this platform/platform margin location (Duvernois et al., 1972; Gaona-Narvaez et al., 2009a). We further estimate the timing and approximate duration of the intervals indicative of oxygen

depletion. Bulk sedimentary rates and duration of individual strata in the section are based on estimated duration of the C-isotope stages during OAE-1a (Li et al., 2008).

4.2. Geographic and Geologic Setting

The Madotz section is located immediately northwest of the town of Madotz (Navarra, sheet #114 Alsasua 1:50000: long. 42°56'24", lat. 1°52'30"), in the southeastern portion of the "Sierra de Aralar", close to the boundaries between the provinces of Guipuzcoa (Basque country) and Navarra (Fig. 4-1).

Figure 4-1 Map showing the location and general geology of the Madotz section. Geologic contacts from Duvernois et al. (1972).

The "Sierra de Aralar" is a western extension of the Spanish Basque Pyrenees in the Basque-Cantabrian region, whose Mesozoic sequence accumulated during the extensional/transensional regime associated with the opening of the North Atlantic Ocean and the Bay of Biscay (García-Mondéjar et al., 1996a; García-Mondéjar et al., 1996b; García-Mondéjar et al., 2004). Folding and uplift of the area developed during subsequent compressional phases in the Paleocene related to the collision between the Iberian and European plates (Rosales et al., 2002). The lithostratigraphic sequence in the Sierra de Aralar includes Uppermost Jurassic

to Barremian limestones, claystones, sandy claystones and sandstones indicative of deltaic conditions succeeded by a widespread Barremian marine unit of organic-rich limestones and mudrocks with *Astarte* (Duvernois et al., 1972). The succession of Aptian and Albian (orbitolinid-rich marlstones, mudrocks and shales), and rudist-rich limestone (Urgonian facies) imply the development of marine conditions and further accumulation on wide carbonate platforms concurrent with the transition from rifting to spreading in the adjacent Biscay Bay (García-Mondéjar et al., 1996a).

Figure 4-2 Aptian stratigraphic context of Madotz series. Chrono and magnetostratigraphy from Ogg and Ogg (2008), ammonite biozones from Reboulet et al. (2012). Lithostratigraphy and orbitolinid biochronology modified from Cherchi and Schroeder (1998).

In the Madotz area the Aptian series has been divided into five units (Duvernois et al., 1972), and the most recent biostratigraphic revision by Cherchi and Schroeder (1998) based on benthic foraminifera can be observed in Figure 4–2. The basal carbonate sequence known as “Madotz Limestone” (“Ensemble II” in Duvernois et al., 1972; Unit 2 in Cherchi and Schroeder, 1998), includes in ascending order (Figs. 4–1, 4–2, 4–3): subunit 2a (coral-algae-bivalve rich limestone), subunit 2b (orbitolinid-rich marlstones), and subunit 2c (rudistid- rich limestone). Carbonate Unit 2 and the fine terrigenous Unit 1 (below the “Madotz Limestone”) have been traditionally correlated with the Lower Aptian (Bedoulian) portion of the *Palorbitolina lenticularis* Zone (Duvernois et al., 1972).

4.3. Materials and Methods

This study includes 62.5 m of the Madotz section (outcrop and trenches), from the top of unit 1 (3 m), units 2a (20 m), 2b (24.4 m), to the basal 15 m of unit 2c of the “Madotz Limestone” (Figs. 4–1 to 4–5).

Initial petrographic and microfacies analyses were carried out on a total of 86 samples. The analyses involved conventional transmitted light microscopy on all the samples, and scanning electron microscopy on selected samples; SEM analyses was conducted with a JEOL JSM 5910LV available at the FIU’S Florida Center for analytical Electron Microscopy (FCAEM). Both at the field scale and microscopic scale special attention was given to the presence/absence of benthic fauna, bioturbation and early diagenetic minerals indicative of redox conditions.

Total inorganic carbon (TIC) and TOC were measured on all samples using a LECO CR-412 carbon analyzer, which uses an infrared cell to measure the CO₂ produced by combustion of 0.250 g of powdered sample in a furnace at 1450°C. Total carbon (TC) and TIC are expressed as a percentage by weight of CaCO₃, whereas TOC values are obtained by subtraction of the former measurements. Here the terms limestone, marlstone, calcareous mudrocks and mudrocks are

Figure 4-3 Panoramic view of subunits 2a and 2b of the Madotz limestone (3A). The outcrop shows the morphological contrast between the orbitolinid calcirudites at the top of Unit 2b and the biomicrites at the base of Unit 2c (3B). Top of the studied section and general view of subunit 2c of the Madotz limestone (3C).

Figure 4-4 Contact between the fine-siliciclastic unit 1 and calcareous subunit 2a, interpreted as a possible sequence boundary (*sb*) (4A). Outcrop at the top of subunit 2a of the Madotz limestone that shows medium and thickly-bedded biocalcarenes and biocalcirudites with scour surfaces (*ss*) and wavy bedding (*wb*) (4B, 4C). Outcrop in the lower part of subunit 2b with medium and thick tabular interbeds of marlstones, calcareous claystones and biocalcilutites poor in fossils (4D). Very thick bed (1.8m) of calcareous claystones and shales representing the longest dysoxic episode in the section, overlain by medium to very thick beds of orbitolinid biocalcirudites (4E). Medium tabular bed (ES-06-40) of orbitolinid calcirudites displaying a scour surface at its base (*ss*) and wavy structures (*wb*) at the top (4F).

based on the relative percentage of total carbonate (measured CaCO_3) as follows: mudrock/shale: 0–10% CaCO_3 ; calcareous mudrock/shale: 10–30% CaCO_3 ; marlstone: 30–60% CaCO_3 ; limestone: >60%).

Carbon isotopic measurements on C_{org} were conducted on 52 samples at the Southeast Environmental Research Center (SERC) using a Finnigan Delta C EA-IRMS (with TC/EA). This technique uses 0.1–1 mg samples of powdered and homogenized dry rock, and reacted with a 1M HCl solution in order to eliminate the inorganic carbon (CaCO_3). The results are reported in δ notation, in parts per thousand (‰) relative to the Vienna Pee Dee Belemnite (VPDB) international standard. Analytical precision for duplicate analyses of standard materials (glycine) revealed standard deviation values from 0.037 to 0.257‰ for $\delta^{13}\text{C}_{\text{org}}$. Analyses of 13 replicate samples of different lithologies produced errors in a range of 0.02 to 0.21‰ for 85% of the samples, and errors in a range of 0.31 to 0.39‰ for 15% of the samples.

4.4. Results

4.4.1. Lithology and Fossil Content

The Lower Aptian Stage at Madotz (Units 1 and 2, Cherchi and Schroeder, 1998) reveals significant temporal variations within the sequence that shows an early stage with terrigenous deposits, followed by “Urgonian” rudist and/or coral-rich limestones, and mudrocks as well as orbitolinid-rich marlstones and limestones.

Unit 1 (0 to 3 m; Figs. 4–4A, 4–5) consists of bioturbated medium gray to olive gray (N5, 5Y 4/1) claystones. At the field scale the fossil association reveals rare shells, either whole or fragmented, of endobenthic bivalves (tellinoids, nuculoids, arcoids), gastropods (Aporrhaidae), ammonites, decapods, wood fragments, and burrows 3–5 mm in diameter (bioturbation index: 3). In Unit 1, TIC varies from 0 to 6.3%, whereas TOC ranges from 0.2 to 0.5%. Unit 1 includes the ammonites *Deshayesites* cf. *forbesi* Casey (Figs. 4–5, 4–6A, 4–6F), and *Pseudohaploceras*? sp.

Unit 2 comprises subunit 2a (3 to 23 m), 2b (23 to 47.4 m), and 2c, respectively:

Subunit 2a is 20 m thick. The basal part, from 3 m to 5.6 m (Fig. 4–4A, 4–5), shows macroscopically and microscopically a transition from the underlying terrigenous facies to predominately carbonate Urganian facies. This interval is poorly exposed and consists of 20–30 cm-thick tabular beds of medium dark gray (N4) biocalcarenites (TIC, 76%; TOC, 0%) with bivalves and benthic foraminifers; dark gray (N3) packed biocalcarenite (TIC, 95.95%; TOC, 0%) with corals and bivalves; and olive gray (5Y 4/1) sparse biomicrudite (TIC, 93.6%; TOC, 0%) with common bivalves and *Palorbitolina lenticularis*.

Subunit 2a continues from 5.6 to 23 m or over a thickness of 17.4 meters (Figs. 4–3A, 4–4B, 4–4C, 4–5), and consists of medium light gray, light olive gray and yellowish gray (N6, 5Y 6/1, 5Y 8/1) nodular, highly recrystallized, packed and sparse biocalcarenite and biocalcirudite (TIC, 85.6%–98.81%) which display mostly wavy-bedding (10–170 cm-thick, Fig. 4–4B-C). Fossil assemblages are composed of corals, sponges, non-rudistid bivalves and echinoderms.

Subunit 2b (Figs. 4–3A-B, 4–4D-F, 4–5) is 24.4 m thick. From 23 to 26.6 m the outcrop was buried under slope wash in a subsequent valley, but we integrate this interval in the basal part of subunit 2b because the valley is indicative of a lithology softer than the infrajacent hard limestone of subunit 2a.

The exposed lower part of subunit 2b (26.6–42.3 m; Figs. 4–3A, 4–4D-F, 4.5), consists in general of 15 to 210 cm-thick interbeds of indurated marly limestones (muddy biocalcirudite, muddy biocalcilutite), bioclastic marlstone, and less indurated interbeds of marlstone, claystone and shale. This part of the section includes different lithologic packets with highly variable TIC and TOC (TIC, 8.16–76.76%; TOC, 0.03–1.35%) that can be described as follows:

From 26.6 to 28.6 m, the beds (28–130 cm-thick) are medium dark gray to olive gray (N4, 5Y 4/1) with wavy primary structures and consist of grain-supported and matrix-supported fine and medium muddy biocalcirudite, as well as planar beds of matrix-supported fossiliferous

marlstone and claystone. These beds also show bioturbation, and a typical fossil assemblage dominated by *Palorbitolina lenticularis* with minor bivalves, echinoderms and brachiopods.

From 28.6 to 36 m, medium dark gray and dark gray (N4, N3) tabular beds (10–110 cm-thick) of bioturbated fossiliferous and sparse calcareous claystone, marlstone and biocalcilitite (Fig. 4–4D, 4–5) which contain scarce bivalves, echinoderms, orbitolinids and ammonites such as *Deshayesites cf. forbesi* Casey (Figs. 4–5, 4–6B), *Pseudosaynella bicurvata* (Michelin) (Figs. 4–5, 4–6C, 4–6G), and *Pseudosaynella raresulcata* (d’Orbigny) (Figs. 4–5, 4–6D). The interval also includes minor interbeds of packed biocalcirudite and bioclastic marlstone rich in the discoidal morphotype of *Palorbitolina lenticularis* (Figs. 4–4F, 4–5). In some fossil-bearing calcareous claystones and silty and sandy claystones, bioturbation is low, and occasionally pyrite occurs randomly scattered throughout with punctual development of nodules; these beds contain rare macrofossils.

From 36 to 37.8 m (Figs. 4–3A, 4–4E, 4–5), the interval is characterized by a remarkable dark gray to grayish black (N3, N2) of bed with calcareous claystone, calcareous clay-shale and clay-shale (TIC, 8.16–18.93%; TOC, 0.56–1.27%) with dispersive framboidal pyrite and relatively enriched in organic matter. The bulk of the 1.8-meter interval shows no apparent bioturbation and rare fossils. Also, the base and topmost contacts (~25 cm-thick) show faint burrows and rare fragments of shallow-water bivalve taxa (e.g. arcoids, cardiids pholadomyoids, and *Neithea* sp.), echinoderms, and ammonites such as *Deshayesites cf. forbesi* Casey (Figs. 4–5, 4–6B) and *Deshayesites* sp. (Figs. 4–5, 4–6E).

From 37.8 to 42.3 m (Figs. 4–3A, 4–4E, 4–5) there is recurrence of thick beds (20–210 cm-thick) of grain-supported fine muddy biocalcirudites, as well as matrix-supported bioclastic marlstone and claystone with the typical assemblage dominated by *Palorbitolina lenticularis*, as those already described in lower levels of subunit 2b (TIC, 14–61.81%; TOC, 0.4–1.27%).

Figure 4-5. Lithology, facies, total inorganic content (weight % CaCO₃), total organic carbon (TOC), stable carbon isotope (δ¹³C_{org}) variations, and ammonite biostratigraphy of the Madotz section. C2-C6 refers to the stable carbon isotope stages defined by Menegatti et al., (1998).

Figure 4–5 continued...

Legend

Bivalves		Bryozoans		Pyrite nodules, fossil infillings		Marlstone
Rudists		Miliolids		Burrows		Claystone
Ammonites		Small benthic forams		Abundant burrows		Clay-shale
Gastropods		Orbitolinids		Chanel shaped structures		Limestone
Corals		Orbitolinid fragments		Cross bedding
Echinoids		<i>Chofatella</i>		Wavy bedding
Crustaceans		<i>Pseudocyclammina</i>		Planar bedding
Ostracod		Calcispheres		Planar lamination
<i>Bueina</i>		Plant fragments
Sponges		Pellets
Brachiopods		Pelloids				

The uppermost part of subunit 2b (42.3–47.4 m; Figs. 4–3B, 4–5) shows another facies change, as it is dominated by bedsets, 60 to 180 cm-thick, with apparent wavy contacts. The rocks are medium gray and medium dark gray (N5, N4), and consist of biocalcirudite, calcarenite and muddy biocalcirudite (TIC, 66.7–97%; TOC, <0.25%). These beds are dominated by *Palorbitolina lenticularis*, including both conical and discoidal morphotypes, and also contain fragments of non rudist bivalves, brachiopods and echinoderms.

Subunit 2c. It forms a prominent ledge known as Madotz Bar (Fig. 4–3C). The lowest part of subunit 2c (47.4 to 52.9 m; Figs. 4–3B, 4–5) consists of 15 to 80 cm-thick beds of medium gray and medium dark gray (N5, N4), calcilutite (TIC, 85.5–89.2%; TOC, <0.1%) and very fine calcarenite with scarce coarse bioclasts, as seen in hand specimens. Primary structures appear as parallel wavy bedding, and locally large-scale cross bedding. Fossil assemblages contain scattered non-rudist bivalves and corals, but orbitolinids are common only at the base of the interval.

The uppermost part of the studied section (52.9 to 62.5 m; Figs. 4–3C, 4–5) represents only the lower portion of subunit 2c (*sensu* Duvernois et al., 1972). The interval studied shows characteristically 10 to 40 cm-thick, medium light gray and light olive gray (N6, 5Y 6/1) fine to medium biocalcirudite beds with wavy contacts. They include scattered fragments of corals,

rudistid and non rudistid bivalves, and brachiopods. They intergrade upward into a 2 m-thick massive bed of sparse calcirudite (floatstone; TIC, 100%; TOC, 0%), with rudists (requieniids).

Requienid-rich facies are found for approximately 85 m more above the studied section (Cherchi and Schroeder, 1998).

4.4.2. Carbon Isotope Ratios

Stable carbon isotope measured on organic matter (OM) at Madotz shows a range of values from -26.5 to -20.6‰, with a time series pattern that allows to distinguish four clear intervals (Fig. 4–5).

The basal 3m of the section corresponding to siliciclastic unit 1 yielded $\delta^{13}\text{C}_{\text{org}}$ values between -23.18‰ and -23.52‰. The overlying 20 m of subunit 2a were not analyzed because TOC was 0%, and farther up sequence 3.6 m of the lowermost part of subunit 2b was unavailable in the outcrop because it was buried under slope wash. Immediately above, the interval of subunit 2b between 26.9 m and 30.4 m shows a trend of ascending $\delta^{13}\text{C}_{\text{org}}$ values from an apparent minimum of -26.5‰ to -22.29‰. The interval between 30.4 m and 37.4 m of subunit 2b displays a group of $\delta^{13}\text{C}_{\text{org}}$ values with minor variability around -22.56‰, followed by a group of descending values from -21.73‰ to -23.95‰ ending as a remarkable negative peak at 40.9 m. The interval from 40.9 m to 49.2 m shows a trend of ascending $\delta^{13}\text{C}_{\text{org}}$ values to a maximum of -20.61‰. This segment includes the top of subunit 2b as well as the base of subunit 2c. The interval between 49.2 and 53.1 m corresponds to the lower part of subunit 2c, which yielded the highest isotopic values of the whole section where $\delta^{13}\text{C}_{\text{org}}$ ranges from -20.61‰ to -21.04‰. The highest TOC values are restricted to the interval between 26.9 and 40.9 m, however the correlation between TOC and stable carbon isotope values is very poor (R^2 , 0.008).

4.5. Biochronology and Biostratigraphy of Madotz Section

4.5.1. Biostratigraphy of OAE-1a

Exact biostratigraphic position of OAE1a has been relatively unsteady due to differences among sites related to the identification of the base of *Leupoldina cabri* Zone. Nonetheless, planktonic foraminifera data from the Tethyan realm and the Pacific suggest that the onset of OAE-1a is placed close to the boundary between the *Blowiella blowi* and the *Leupoldina cabri* zones, and that the event itself extends within the lowest part of the *Leupoldina cabri* biozone (Moullade et al., 1998; Cobianchi et al., 1999; Erba et al., 1999; Strasser et al., 2001; de Gea et al., 2003; Heldt et al., 2008), see also Figures 4–8 and 4–9. Correlation of OAE-1a with ammonite has been controversial as many authors (e.g. Föllmi and Gainon, 2008; Embry et al., 2010) placed the event within the *Deshayesites deshayesi* Zone (see Fig. 4–2) in agreement with the biostratigraphic interpretation of Moullade et al. (1998) who used ammonites data from SE France to correlate OAE-1a with the *Roloboceras hambrovi* Subzone, which was believed to correspond to the lower part of the *Deshayesites deshayesi* Zone. However, additional ammonite biostratigraphic and carbon isotope data from multiple sections in the Iberian Peninsula (Moreno-Bedmar et al., 2009; Moreno-Bedmar, 2010), permit to correlate the *Roloboceras hambrovi* Subzone with the upper part of the *Deshayesites forbesi* Zone, formerly *Deshayesites weissii* Zone (Reboulet et al., 2012). Therefore, OAE-1a is now placed in the infrajacent *Deshayesites forbesi* Zone. This biochronological interpretation of OAE-1a within the *Deshayesites forbesi* Zone (Moreno-Bedmar et al., 2009; Moreno-Bedmar, 2010; Reboulet et al., 2012), is also in agreement with the biochronologic position of the onset of the nannoconid crisis (Aguado et al., 1999; de Gea et al., 2003; Najarro et al., 2011), and the FAD of *Leupoldina cabri* (Aguado et al., 1999; de Gea et al., 2003); see also Figs. 4–7 to 4–9.

4.5.2. Benthic Foraminifer Biochronology of Madotz Section

Biochronology of the Madotz section was previously determined (Duvernois et al., 1972; Cherchi and Schroeder, 1998) based on benthic foraminifers, which includes abundant specimens of *Palorbitolina lenticularis*, *Choffatella decipiens* and *Pseudocyclammina hedbergi* in levels from the top of unit 1 to the base of unit 2c (Fig. 4–2). In the Mediterranean region, these taxa coexist between the upper Barremian and lowest Gargasian (Luperto Sinni, 1979; Bachmann and Willems, 1996), therefore this time range is too broad for the biochronologic resolution needed for the purpose of this work.

Cherchi and Schroeder (1998) dated subunit 2c and levels above the limit of our study as Late Aptian (Middle Aptian, *sensu* Reboulet, 2012, equivalent approximately to the Gargasian) based on the presence of *Orbitolinopsis simplex*, which (Moullade et al., 1985) reported in the lowest part of the Gargasian. Subsequent studies (Bover-Arnal et al., 2010) also recorded *Orbitolinopsis simplex* from the terminal part of the Bedoulian corresponding to the *Dufrenoyia furcata* Zone. Assuming that these reported ranges are valid, the reliability of *Orbitolinopsis simplex* to accurately constrain the time in subunit 2c remains an open question since the Gargasian would apparently include the *Dufrenoyia furcata* ammonite biozone (see further discussion in Reboulet et al., 2006).

4.5.3. Ammonite Biochronology of Madotz Section

Our study of the Madotz section yielded new ammonite specimens of *Deshayesites* cf. *forbesi* and the genus *Pseudosaynella*. The presence of *Deshayesites* cf. *forbesi* in unit 1 (0–3.7 m) and subunit 2b (lower 14.7 m), the first appearance datum of *Pseudosaynella* in subunit 2b, and the high relative abundance of *Pseudosaynella* specimens, support a stratigraphic position correlative with at least the upper part of the *Deshayesites forbesi* Zone (Moreno-Bedmar et al., 2009), although bistratigraphic data are scarce and no boundaries were found. The new ammonite data at Madotz are in agreement with observations by other authors concerning the first

Figure 4-6. Lower Aptian ammonite specimens collected at Madotz. Unit 1: *Deshayesites* cf. *forbesi* Casey (Figs. A, F). Subunit 2b: *Deshayesites* cf. *forbesi* Casey (Fig. B), *Deshayesites* sp. (Fig. E), *Pseudosaynella bicurvata* (Michelin) (Fig. C) and *Pseudosaynella raresulcata* (d'Orbigny) (Fig. D).

appearance of *Pseudosaynella* specimens (Casey, 1961; Grauges et al., 2010), as well as its abundance in the upper part of the *Deshayesites forbesi* Zone (Moreno-Bedmar et al., 2007), thus corroborating a lower stratigraphic position for the section in the early Bedoulian (Gaona-Narvaez et al., 2009a; Gaona-Narvaez et al., 2009b; see also fig. 5).

In works by precedent authors ammonites were reported only in Unit 1 of the section, and the specimens were assigned to *Deshayesites deshayesi* (Duvernois et al., 1972). Such designation would indicate a stratigraphic level within the *Deshayesites deshayesi* Zone corresponding to the upper part of the Bedoulian, and above the *Roloboceras hambrovi* subzone of the *Deshayesites forbesi* Zone where recent consensus placed the interval of occurrence of OAE1a (Reboulet et al., 2012). The specimen of *D. deshayesi* previously reported in Unit 1 (Duvernois et al., 1972) may be considered a misidentified taxon.

4.6. Correlation Between Biostratigraphy and Isotope Stratigraphy of OAE-1a at Madotz Section

The time series for $\delta^{13}\text{C}_{\text{org}}$ curve of subunit 2b, between 26.6 and 49.2 m (Fig. 4–5) corresponding with the *Deshayesites forbesi* zone, shows two excursions of 4.21‰ and 3.34‰, separated by an intervening segment with more uniform values around -22.56‰. These two positive excursions are correlational with segments C4 and C6 of OAE-1a, whereas the intervening segment is correlated with segment C5 (Gaona-Narvaez et al., 2010), as defined by Menegatti et al. (1998) on the temporal distribution of $\delta^{13}\text{C}_{\text{org}}$ in the Cismon section (Italy), further confirmed in multiple worldwide locations (Figs. 4–8 and 4–9).

Chemostratigraphic correlation of the Madotz $\delta^{13}\text{C}$ curve with extended hemipelagic sections in the Maestrat basin and the Prebetic domain (Spain), which contain more complete ammonite and isotopic records, bring further clarification about the stratigraphic equivalence of the upper part of subunit 2b and the base of unit 2c that lack biochronologically significant bioevents. Calibration of ammonite zones and $\delta^{13}\text{C}_{\text{carb}}$ in the hemipelagic sections of Barranco de

las Calzadas, Cap de Vinyet, Cau and Raco Amplé (de Gea et al., 2003; Moreno-Bedmar et al., 2009; Moreno-Bedmar et al., 2010; Moreno-Bedmar et al., 2012) indicates that the *D. forbesi* Zone ranges from the uppermost part of $\delta^{13}\text{C}_{\text{carb}}$ segment C2 to the lowest part of segment C7 (Fig. 4–7). Based on these correlations the carbon isotope data at Madotz indicate the following:

- The top of the terrigenous unit 1 that is part of the *Deshayesites forbesi* Zone is most likely correlative with carbon isotope segment C2, as it shows $\delta^{13}\text{C}_{\text{org}}$ values from -23.18 to -23.52‰ (Figs. 4–5, 4–7).

Figure 4-7 Comparison of stable carbon isotope stages and the Tethyan Lower Aptian ammonite biozones in four sections in the Iberian Peninsula: Madotz (this work), Cau (de Gea et al., 2003; Moreno-Bedmar et al., 2012), Barranco de las Calzadas (Moreno-Bedmar et al., 2009), and Cap de Vinyet sections (Moreno-Bedmar et al., 2009). The last two sections put in evidence that the lowest part of stable carbon isotope stage C7 coincides with the terminal part of the *Deshayesites forbesi* zone, and thus the upper part of subunit 2b and the base of subunit 2c in the studied section at Madotz. Selected bioevents are shown for reference.

- The position of the negative isotopic excursion (stage C3) is uncertain, it could be located either in the covered lowest 3.5 m of subunit 2b, or in infrajacent shallow water carbonate subunit 2a, which also belongs in the *Deshayesites forbesi* Zone (see further discussion in section seven of the paper).
- The interval that includes subunit 2b showing chemostratigraphic correlations with $\delta^{13}\text{C}_{\text{org}}$ segments C4 to C6 (26.9–49.2 m, Figs. 4–5 and 4–7), which is the stratigraphic equivalent of OAE-1a, could be situated entirely in the *Deshayesites forbesi* Zone.
- The interval lacking ammonites between 37.7 m and 53.1 m, which includes the upper part of subunit 2b and the basal few meters of subunit 2c below the rudistid limestone, is correlative to C-isotope segments C6 and the base of C7. Therefore, it may be correlative to the *Deshayesites forbesi* Zone (see Figs. 4–5 and 4–7).

4.7. Sedimentary Rates During OAE-1 in Madotz Section

The calculation of bulk sedimentary rates in the Madotz section is based on the duration of OAE-1 $\delta^{13}\text{C}_{\text{org}}$ stages established by Li et al. (2008) from the Santa Rosa Canyon section (Mexico) by integration of orbital cycles and magnetostratigraphy (C4+C5:~930 kyr, C6:~310 kyr). Bulk sedimentary rates at Madotz were calculated with two possibilities, with and without the assumption that the covered 3.6 m-thick outcrops at the base of lithological segment 2b are part of organic carbon isotope stage C4. In consequence, average sedimentation rates in the section during isotopic stages C4+C5 and C6 are ~1.5 to 1.89 cm/kyr and ~2.68 cm/kyr, respectively

The record of OAE-1a at Madotz with a bulk sedimentary rate from 1.8 to 2.09 cm/kyr for C-stages C4 to C6, is an expanded series when compared to the pelagic Cismon Apticore (0.31 to 0.34 cm/ky; Li et al., 2008), but show similar sedimentation rate to the hemipelagic section of the Santa Rosa Canyon (2.07 cm/kyr to 2.19 cm/kyr; Li et al., 2008).

Assuming a duration of 44 kyr for C3 (Li et al., 2008), and bulk sedimentary rates between 1.8 to 2.09 cm/kyr, the estimated thickness of the prominent negative carbon isotope excursion at the beginning of OAE-1a, which is associated with C-stage C3, is calculated to be 79 to 92 cm in the Madotz section. The drastic reduction of carbonate content in the section from lithologic segment 2a to 2b would also suggest that the negative isotope excursion C3 is placed in the lowest covered part of lithologic segment 2b.

4.8. Evidence for Hypoxic Episodes and their Duration in the Madotz Section

The lower part of subunit 2b of the Madotz section is dominated by carbonate-terrigenous mixed facies (muddy biomicrudites, biolutites, marlstones, calcareous claystones), generally bioturbated and containing macro and microfossils characterized by either orbitolinid-bivalve-echinoderm, or bivalve-echinoderm-*Choffatella* assemblage (Fig. 4–5); these facies are interpreted to be deposited in fully oxygenated bottoms (Gaona-Narvaez et al., 2009a).

These levels are interbedded with at least four intervals (25–43 cm-thick; between 26.6 and 36 m) of marly limestones, marlstones and calcareous claystones (TOC, 0.22–0.8%; TIC, 14–64%) that contain framboidal and nodular pyrite. They also contain rare benthic fossils (littolids, orbitolinid, ostracods), calcispheres, and show low bioturbation. These intervals can be related to conditions of episodic hypoxia, thus pyrite was mostly concentrated in anoxic microenvironments created by decay of organic matter disseminated in the matrix and in fossil chambers. The calculated duration for these hypoxic intervals is between 13.2 and 22.7 kyr assuming bulk sedimentary rate of 1.5 to 1.89 cm/kyr.

The most prominent development of facies indicative of oxygen depletion is represented by a 1.8 m-thick bed (36 to 37.8 m) of pyritic calcareous claystone, calcareous clay-shale and clay-shale with TOC from 0.52 to 1.27%, and TIC from 8.16 to 18.93% (Fig. 4–5).

Figure 4-8 Chemostratigraphic correlation of the fine-grained siliciclastic interval (subunit 2b) of the Madotz section (broken red line, this work) with other sections in the Iberian Peninsula (de Gea et al., 2003; data after de Gea et al., 2008a; Millán et al., 2009; Moreno-Bedmar et al., 2009; Moreno-Bedmar, 2010; Moreno-Bedmar et al., 2012). This interval contains clay-shales and claystones interpreted as deposited under oxygen-deficient conditions in the studied section.

Figure 4-9 Chemostratigraphic correlation of the fine-grained siliciclastic interval (subunit 2b) of the Madotz section (broken red line) with other sections in the Tethyan Realm (Menegatti et al., 1998; Erba et al., 1999; Channell et al., 2000; Bellanca et al., 2002; Immenhauser et al., 2005; Heldt et al., 2008). This interval contains clay-shales and claystones interpreted as deposited under oxygen-deficient conditions in the studied section

Most of the thickness is characterized by absence of bioturbation scarce ostracods and calcispheres (Gaona-Narvaez et al., 2009a). The inferred duration for this bed is 95.23 to 120 kyr assuming bulk sedimentary rate of 1.5 to 1.89cm/kyr. Because both the base and top of this bed (~25 cm-thick) show faint burrows and rare fragments of shallow-water taxa, such as bivalves and echinoderms, the bed includes more than a cycle of oxygenation and oxygen depletion. We interpret these beds to have been deposited in outer platform/ramp environment at the time of C-isotope stages C4 and C5 (~ 900 to 930 kyr, Li et al., 2008).

In contrast, the upper part of subunit 2b, and the base of subunit 2c are characterized by carbonate/terrigenous facies (orbitolinid-rich biomicrudites, calcarenites, and marlstones), and carbonate facies (lituolid-miliolid-bivalve biomicrites and biopelmicrites, foraminifer-rudist-coral biomicrudites and rudistid biomicrites) with abundant benthic fossils and poor in TOC. These deposits are interpreted to represent fully oxygenated conditions in platform margin and lagoonal environments. They comprise $\delta^{13}\text{C}_{\text{org}}$ segment C6 (~300 to 330 kyr, Li et al., 2008), and the base of $\delta^{13}\text{C}_{\text{org}}$ segment C7, respectively.

The short vertical extent of the relatively organic-rich shale and claystone at Madotz, which encloses only C-isotope stages C4 and C5 of OAE-1a, contrasts with the apparent longer temporal extent of the organic-rich shale in hemipelagic and pelagic settings. As observed in Figures 8 and 9, the extent of organic-rich facies in sections of hemipelagic and pelagic settings may range from the upper part of $\delta^{13}\text{C}_{\text{carb}}$ stage C2 to the lowest part of C7 (e.g. Menegatti et al., 1998; Erba et al., 1999; Bellanca et al., 2002; de Gea et al., 2003; de Gea et al., 2008a; Heldt et al., 2008).

Slight heterochrony in the distribution of organic-rich facies during OAE's when calibrated to the carbon isotope record was also remarked by Tsikos et al. (2004) in areas outside of the Atlantic during OAE-2. In that sense our work supports the point made by Jenkyns (2010)

regarding the value of the carbon isotope curve as a descriptor of OAE's rather than the presence of organic-rich layers.

4.9. Conclusions

Based on new chemostratigraphic and biostratigraphic data available from the Madotz section, the time interval equivalent to OAE-1a corresponds to the whole vertical extent of subunit 2b (24.4m) in which C-isotope stages C4 to C6 were identified. Subunit 2b correlates with the upper part of the Lower Aptian *Deshayesites forbesi* biozone, which is in agreement with the age of OAE-1a at other locations of the Iberian Peninsula.

Deposits within the time interval of OAE-1a in the studied section are represented by mixed carbonate/terrigenous sediments dominated by low diversity orbitolinid-rich facies, with punctual development of pyritic claystone, and clay-shale beds relatively rich in OM. We calculated a bulk sedimentation rate from 1.8 to 2.09 cm/kyr for this local record of OAE-1a, between C-isotope stages C4 and C6.

Facies indicative of oxygen depletion conditions are restricted to C-isotope stages C4 and C5, the later includes a main level of prevalent disoxia with maximum duration of about 95.23 to 120 kyr. Thus, at Madotz the temporal extent of relatively OM-rich facies indicative of oxygen depletion during OAE-1a in the outer ramp/platform setting (subunit 2b) is shorter than reported elsewhere for organic-rich shale facies in pelagic and hemipelagic environments.

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5 GEOCHEMISTRY, PALEOENVIRONMENTS AND TIMING OF APTIAN ORGANIC-RICH BEDS OF PAJA FORMATION (CURITÍ, EASTERN CORDILLERA, COLOMBIA)

Gaona-Narvaez, T., Maurrasse, F. J.-M.R., Etayo-Serna F., 2013. Geochemistry, paleoenvironment and timing of Aptian organic-rich beds of Paja Formation (Curití, Eastern Cordillera, Colombia). In: Bojar, A.-V., Melinte-Dobrinescu, M.C., Smit, J. (Eds.), *Isotopic Studies in Cretaceous Research*. Geological Society, London, Special Publications, 382, <http://dx.doi.org/10.1144/SP382.6> Article in press.

Abstract

At the Curití Quarry, Eastern Cordillera of Colombia, a 23.35 m section includes a 6.3-m-thick interval of organic-rich marlstones, calcareous clay-shales and clay-shales devoid of benthic fossils and bioturbation, at the base of the Paja Fm. It overlies carbonate ramp deposits of the Rosablanca Fm with the topmost layer containing reworked and phosphatized assemblages of middle Barremian to lowest Aptian ammonites of the genera *Pulchellia*, *Gerhardtia*, *Toxancycloceras*, *Karsteniceras* and *Prodeshayesites*. High-resolution analyses of the section, including total inorganic carbon (TIC, 0.09–50 wt%), total organic carbon (TOC, up to 8.4%), and stable carbon isotope measurements ($\delta^{13}\text{C}_{\text{org}}$ between -22.05‰ and -20.47‰), allow to determine the stratigraphic relationship between the organic-rich level within the Paja Formation and Oceanic Anoxic Event 1a (OAE-1a.). The range of values and the overall pattern of the $\delta^{13}\text{C}_{\text{org}}$ curve is comparable with the Lower Aptian interval C7. Thus the organic-rich shale interval of the Paja Fm at the Curití section, showing characteristics of oxygen depleted conditions, was deposited after OAE-1a, which is known to occur between isotopic levels C3 and C6.

5.1 Introduction

The widespread record of Cretaceous marine black shales characteristic of Oceanic Anoxic Events (OAE's) has been related to enhanced preservation of organic matter in sedimentary basins that led to major perturbations in the global carbon cycle and recognizable carbon isotopic excursions

The perturbation of the carbon cycle that occurred in the Early Aptian known as Oceanic Anoxic Event 1a (OAE-1a, Arthur *et al.* 1990), is reported to have lasted between 1.0 and 1.3 Ma (Li *et al.* 2008) and to coincide in the Tethyan domain with the lower part of the *Leupoldina cabri* planktonic foraminiferal zone (Erba *et al.* 1999), and the upper part of the *Deshayesites forbesi* ammonite Zone (Moreno-Bedmar *et al.* 2009; Moreno-Bedmar *et al.* 2010; Moreno-Bedmar *et al.* 2012; Reboulet *et al.* 2012). OAE-1a is characterized by a widespread deep sea anoxia that developed in a global context of intense volcanic activity in the Pacific (Larson 1991; Méhay *et al.* 2009; Tejada *et al.* 2009), high oceanic surface water temperatures with a reduced equator to poles thermal gradient (Frakes 1999; Pucéat *et al.* 2003), and generalized high sea level (Haq *et al.* 1987; Skelton 2003), as well as increased marine primary productivity (Dumitrescu & Brassell 2005; Luciani *et al.* 2006; de Gea *et al.* 2008b; Heldt *et al.* 2008). The overall global carbon isotopic signature of OAE-1a has been identified by a strong negative peak (stage C3), followed by two rapid positive excursions (stages C4 and C6) separated by a period of high constant isotopic values (C5) (Menegatti *et al.* 1998). However, the interval with the highest $\delta^{13}\text{C}_{\text{carb}}$ values recorded during the Aptian coincides with isotopic stage C7 in the upper part of the *Leupoldina cabri* planktonic foraminiferal zone (Menegatti *et al.* 1998; Bralower *et al.* 1999; de Gea *et al.* 2003).

In addition to organic-rich shale levels associated with OAE-1a in western Europe (Goguel, Selli, Fischschiefer levels), localized organic-rich shales are also associated with intervals C7 and C8 in the Vocontian Basin (Noire and Fallot levels; Herrle *et al.* 2004; Herrle *et al.* 2010), the Gargano Promontory (Luciani *et al.* 2006), the Basque-Cantabrian region (Millán *et al.* 2008), the Prebetic and Subbetic ranges (de Gea *et al.* 2003; de Gea *et al.* 2008a).

Despite variability of the carbon isotope signal observed between shallow, hemipelagic and pelagic settings (e.g. Burla *et al.* 2008), the pattern of temporal distribution of the stable carbon isotope values is consistent with well-established biostratigraphic zones that provide

reliable references for chemostratigraphic correlation within Lower and middle Aptian series. Conjoint uses of these sets of data has the potential to help clarifying the context of organic-rich intervals in local basins, as they may not necessarily be linked to more widespread global perturbations in the carbon cycle.

In the present work, we studied the Aptian organic-rich interval in the lowest part of the Paja Fm, which overlies the Barremian-age carbonate ramp deposits of the Rosablanca Fm at the Curití section in Colombia (Eastern Cordillera). We use a multi-proxy approach that includes the integration of stable carbon isotopes ($\delta^{13}\text{C}_{\text{org}}$), total organic carbon (TOC) and total inorganic carbon content (TIC), as well as ammonite biochronology in order to determine the relationship between the organic-rich interval at the base of the Paja Fm and the Lower Aptian OAE-1a (~120 Ma) or its occurrence as younger regional event.

5.2 Geological Setting and Previous Studies

The **Curití section** is an active quarry (Cementos Argos Quarry, formerly Cementos Hercules, lat. 6°36'58" N, long. 73°4'32" W) in the area adjacent to the town of Curití (San Gil-Bucaramanga road, Santander), in the Colombian Eastern Cordillera (Figs. 5–1, 5–2). The studied section was part of the Mesozoic Tablazo-Magdalena basin (TMB), interpreted as a rift system oriented NNE-SSW, and limited to the east by a system of horst blocks in the area of the Santander-Floresta Massif (Etayo-Serna *et al.* 1976; Fabre 1987; Etayo-Serna *et al.* 2003). The Tablazo-Magdalena Basin was bounded to the west by the Palestina Fault of the Central Cordillera. Early syn-rift fluvial and lacustrine deposits recorded two stretching events between the latest Triassic and Mid-Jurassic. Subsequent marine transgression in the basin between the Berriasian and the middle Aptian progressed in a N-NE direction that led to the accumulation of heterochronous siliciclastic and evaporite/carbonate series in littoral and shelf environments (Etayo-Serna *et al.* 1976; Allen *et al.* 1988; Rolón & Carrero 1996; Sarmiento 2001; Rolón 2004).

These deposits involve at least three third-order sequences (Rolón & Carrero 1996), as sedimentation in the TMB was controlled by tectonic subsidence until the Aptian (Sarmiento 2001; Rolón 2004). Maximum sea levels are recorded in the early Late Valanginian, Early to middle Barremian, and Late Aptian; in contrast, eustatic changes controlled the basin infilling for most of the mid- and Late Cretaceous (Rolón & Carrero 1996; Sarmiento 2001; Rolón 2004). The Mesozoic extensional TMB was modified into a retroarc foreland basin at the end of the Cretaceous (Campanian-Early Paleocene) by episodes of uplift in the Central Cordillera (Restrepo-Pace *et al.* 2004; Gómez *et al.* 2005). Further evolution includes Paleocene-Early

Figure 5-1 Map showing the location of the Cutití section and its regional structural context (modified from Gómez *et al.* 2007).

Eocene thrusting in the area of present Middle Magdalena Valley (MMV) and the western flank of the Eastern Cordillera, as well as subsequent basin inversion and uplift of the Eastern Cordillera during the Miocene-Pliocene (Sarmiento 2001; Restrepo-Pace *et al.* 2004; Barrero *et al.* 2007).

Areas close to the western border of the Santander Massif such as Curití and La Mesa de los Santos include a more complete record of the Berriasian alluvial systems and the earliest Cretaceous transgression over the Los Santos Formation (Zamarreño de Julivert 1963; Alfonso 1985; Guzmán 1985; Laverde 1985; Laverde & Clavijo 1985). Shallow water carbonate sedimentation represented by the Rosablanca Formation developed in the Valanginian with local deposits of transgressive evaporitic facies, followed by a long-term regressive succession of fine-carbonate and mixed carbonate/terrigenous deposits mostly Valanginian and Hauterivian in age in the Mesa de los Santos (Zamarreño de Julivert 1963; Alfonso 1985; Guzmán 1985; Cadena 2011). Carbonate sedimentation was clearly interrupted in some shallow locations during the Late Hauterivian with local deposits of continental facies (e.g. northern areas of La Mesa de los Santos). Carbonate sediments of the Rosablanca Fm. accumulated during the Barremian, and at Curití the end of the carbonate platform is marked by deposits of organic-rich black shales and micrites of the Aptian Paja Formation.

5.3 Materials and Methods

Our study includes the integration of field descriptions, Total Inorganic Carbon (TIC), Total Organic Carbon (TOC) and stable carbon isotope measurements ($\delta^{13}\text{C}_{\text{org}}$), and ammonite biostratigraphy at the “Cementos Argos” Quarry at Curití (here Curití Section, Figs. 5–1, 5–2). It includes a detailed geochemical analysis of 1.56 m of the Rosablanca Fm and 7.3 m of the superjacent Paja Fm, out of a total of 23.35 m of section described in the field (Figs. 5–3, 5–5).

Biostratigraphic control was based on *in-situ* specimens collected during this study as well as on specimens previously collected by the Colombian Geological Survey on the same

section. All paleontological collections have been deposited at the José Royo y Gómez Paleontological Museum in Bogotá (Colombia).

Figure 5-2 Panoramic view of the studied section at Curití Quarry on the road from San Gil to the town of Curití (2a). The outcrop shows lithological contrast between the Rosablanca and Paja formations, and the interval of geochemical study (2b). Labels indicate position of beds mentioned in the stratigraphic log and text.

Petrographic analyses were carried out on a total of 78 samples, examined under conventional transmitted light microscopy on all the samples, and on selected samples SEM analyses were conducted with a JEOL JSM 5910LV available at the FIU Florida Center for Analytical Electron Microscopy (FCAEM). Both at the field scale and the microscopic scale special attention was given to the presence/absence of benthic fauna, bioturbation and early diagenetic minerals indicative of redox conditions.

Total inorganic carbon (TIC) and total organic carbon (TOC) were measured on all samples using a LECO CR-412 carbon analyzer, which uses an infrared cell to measure the CO₂ produced by combustion of 0.250 g of powdered sample in a furnace at 1450°C. Total carbon (TC) and TIC are expressed as a percentage by weight of CaCO₃, whereas TOC values are obtained by subtraction of the former measurements.

Here the terms limestone, marlstone, calcareous mudrock and mudrock are based on the relative percentage of total carbonate (measured CaCO₃) as follows: mudrock/shale, 0–10% CaCO₃; calcareous mudrock/shale, 10–30% CaCO₃; marlstone, 30–60% CaCO₃; limestone, >60% CaCO₃).

Pyrolysis on total rock sample was performed on seven samples representative of all fine-grained lithologic types present in the section, using a ROCK-EVAL II-PLUS analyzer (Vinci Technologies) in the Center of Petroleum Geochemistry at the University of Houston. The following parameters were obtained in order to define the degree of maturity of organic matter: free hydrocarbons (S1), generatable hydrocarbons (S2), generatable carbon dioxide (S3), Tmax, hydrogen enrichment index (HI=S2/TOC*100), and oxygen enrichment index (OI=S3/TOC*100).

Carbon isotopic measurements on C_{org} were conducted on 77 samples at the Southeast Environmental Research Center (SERC) using a Finnigan Delta C EA-IRMS (with TC/EA, temperature conversion elemental analysis). This technique uses 0.1–1 mg samples of powdered

and homogenized dry rock, and reacted with a 1M HCl solution in order to eliminate the inorganic carbon (CaCO₃). The results are reported in δ notation, in parts per thousand (‰) relative to the Vienna Pee Dee Belemnite (VPDB) international standard. Analytical precision for duplicate analyses of standard materials (glycine) revealed standard deviation values from 0.035‰ to 0.086‰ for $\delta^{13}\text{C}_{\text{org}}$. Analyses of 15 replicate samples of different lithologies produced errors in a range of 0 to 0.09‰, but only 6.6% of the samples display an error <0.086‰.

5.4 Results

5.4.1 Lithology and Fossil Content

The 23.3-m studied section at Curití includes the top 1.56 m of the carbonate series of the Rosablanca Formation with its topmost 17cm consisting of a conspicuous phosphatic bed. The Rosablanca Fm is overlain by 21.8 m of black shales and marlstones that constitute part of the Paja Fm (Figs. 5–2, 5–3).

5.4.1.1 *Rosablanca Fm*

On the overall, the 1.56-m interval of the Rosablanca Fm studied at Curití shows a carbonate unit that experienced rapid lithological change, from packed biocalcirudites (packstones and wackestones) to biomicrites (calcimudstones, Fig. 5–4g) that show gradual increase in the content of organic matter and phosphate. The carbonate unit of the sequence is sharply interrupted by a 17cm-thick calcareous and pyritic phosphorite (packstone, Fig. 5–4h) as a boundary bed between the two formations.

In detail, the interval studied starts with 96 cm of dark gray, medium and thick tabular beds (12–38 cm) of poorly sorted, packed, bivalve-rich biomicrudites (packstone; TIC, 67.2–93.8%; TOC, 0.04–0.6%). This facies comprises articulated and inarticulated shells of shallow-water bivalve taxa (trigonids, arcids, heterodonts), rare ammonites and rounded phosphatic pebbles.

Figure 5-3 Lithology and ammonite content at the Curití section.

Figure 5-4 Marlstone displaying fine carbonate-rich and organic-rich interlaminae that include dispersed dolomite crystals (*Dol*), Paja Fm, sample Co-09-37 (a). Micritic limestone with fish bone fragments (*Fr*), Lower Aptian Paja Fm, sample Co-09-30 (b). Marlstone displaying wavy laminae, phosphatic remains and bivalves (*Biv*), Lower Aptian Paja Fm, sample Co-09-25b (c). Highly recrystallized limestone, Lower Aptian Paja Fm, sample Co-09-17b (d). Pelmicrite associated with concretion levels, allochems include coproliths (*Copr*), Lower Aptian Paja Fm, sample Co-09-14 (e). Organic-rich black shale with fish bone fragments (*Fr*) and dispersed dolomite, base of Paja Fm, Lower Aptian, sample Co-09-7 (f). Micritic limestone with fish bone fragments (*Fr*), mid-Barremian Rosablanca Fm, sample Co-09-6a (g). Condensed mid Barremian to Lower Aptian phosphatic bed including abundant fish bones (*Fr*) and other phosphatized particles (*Ph*), top of Rosablanca Fm, sample Co-09-6b (h).

These beds include conspicuous undulating laminae, as well as imbrication and nesting of bioclasts, and its top consists of a 3cm-thick muddy dolomitic calcarenite (wackestone with undulating structure) rich in undifferentiated phosphatic intraclasts and fish bones.

Between 0.96 and 1.39 m tabular beds (13–29 cm thick beds) consist of black calcilutites (Fig. 5–4g). Microscopically they correspond to fossiliferous micrites/calcmudstones with fish bones, echinoderm fragments, and phosphatic intraclasts (TIC, 61.4–81.3%; TOC, 0.4–0.7%).

The top 17 cm of the unit that consists of calcareous and pyritic phosphorite (packstone; TIC, 64.6%; TOC, 0.16%; P, 4.2%; Figs. 5–4H and 5–5), displays an irregular basal contact, irregular wavy laminae, and abundant, very poorly sorted fossil components. Fossils include phosphatic steinkerns of articulated lucinid bivalves and ammonites (up to 50 cm in diameter), phosphatized fish remains, as well as permineralized (carbonate) wood fragments, and recrystallized bivalve shells. Bioclastic materials include well-preserved shells as well as fossils with different degrees of alteration (bioerosion).

5.4.1.2 Paja Fm

The studied 21.8 m sequence of the Paja Fm (Figs. 5–2, 5–3) is mostly composed of tabular, partly indurated, organic-rich, black clay-shales, calcareous clay-shales and marlstones, interbedded with indurated tabular and lenticular beds of black, non-fossiliferous, and fossiliferous calcimudstones. The sequence includes fifteen (15) levels with concretions.

The basal 6.3-m interval of the Paja Fm, between 1.56 and 7.87 m from the base of the section (Figs. 5–3, 5–5), is dominated by interbeds of two types of partly indurated layers. The first group includes black clay-shales, calcareous clay-shales and marlstones (TIC, 0–50.7%; TOC, 0.5–8.8%; Fig. 5–4f) that display even, parallel laminae and no bioturbation. The other type consists of 7–22 cm-thick of muddy crystalline limestones with apparent wavy lamination (TIC, 69.5–80%; TOC, 1.16–3.9%; Fig. 5–4d). Hard interbeds of calcilutites are black and less

frequent. They are tabular and lenticular, show rare or no bioturbation and vary from 4 to 40cm in thickness (TIC, 72.8–86.3%; TOC, 1.3–1.7%).

Microscopically, the marlstones, clay-shales, and calcareous clay-shales consist of micrite and OM-rich interlaminae. These facies contain rare fossils (up to 10%) such as calcispheres, fish bones and scales, ostracods, planktonic foraminifera, and bivalve together with echinoderm fragments at certain levels. Dolomitic crystals may develop around the calcareous fossils (Fig. 5–4f). Disseminated framboidal pyrite is present in the matrix, or within fossils. The calcareous shales and marlstones include five levels of centimeter-to decimeter-sized concretions (TIC>88%; TOC, 0.17–0.7) composed of calcilutites (pelmicrites). The concretions show abundant crustacean fecal pellets (Fig. 5–4e), rare ostracods, benthic foraminifera, fish bones, and ammonite fragments. The muddy crystalline limestones show high degree of recrystallization, but include rare calcispheres, as well as minor pyrite and rhombic crystals of dolomite. The black limestone interbeds consist of calcilutites (calcimudstones) and contain rare fossils (calcispheres and ostracods), as well as disseminated pyrite and rhombic dolomite crystals.

The interval from 6.31 to 14.94 meters of the Paja Fm, between 7.87 and 16.5 m from the base of the section (Figs. 5–3, 5–5), is characterized by high-frequency, interbedded, black calcareous clay shales and marlstones (TIC, 6.7–51%; TOC, 2.3–5.1%), 12–80 cm thick, as well as hard tabular lenticular and concretionary calcilutites (7–52 cm-thick; TIC, 65.13–94.4%; TOC, 0.64–3.32%; Fig. 5–4b). Also, there are rare, tabular levels of black biocalcilutites with poorly sorted, phosphatized bivalve and gastropod shells (juvenile). At 7.35 m from the base of the unit and 8.91 m from the base of the section (bed 31) concretions appear imbricated and consist of biomicrites (wackestone) with ammonites and bivalves. The interval also includes minor interbeds (3.5–18 cm-thick) of phosphatic, fossiliferous marlstones (P up to 0.6%) with wavy interlaminae and poorly sorted phosphatic intraclasts, fish bones and bivalve fragments (Fig. 5–4c).

Microscopically, the black calcareous clay shales and marlstones contain calcispheres, phosphatic fish fragments, and occasional inoceramids. Bioturbation is low to absent. In the marlstones, even, parallel interlaminae formed by micrite-rich /organic-rich couplets are most conspicuous (Fig. 5–4a). Pyrite is present as disseminated framboids, small nodules, and as rims around three-dimensional fossils within micritic concretions. The tabular levels of black, sparse biomicrites (wackestones) also include poorly sorted, phosphatized bivalve shells, gastropods and ammonites.

The interval from 14.94 to 19.43 m of the Paja Fm, between 16.5 and 20.99 m from the base of the section (Fig. 5–3), is composed of tabular beds of black marlstones and calcareous shales, and shales (4–70 cm thick; TIC, 0–48%; TOC, 1.2–5.4%), interbedded with tabular and lenticular calcilutites (5–30 cm thick; TIC, 87–91%; TOC, 0.5–0.8%). The interval also includes tabular levels of biocalcirudites (pelbiomicrudite, wackestones) and biocalcilutite concretions that contain mostly bivalves, as well as rare ammonites and gastropods. The marlstones and calcareous clay shales contain less than 10% fossils, which include phosphatic fish bones, small sized bivalves and inoceramids visible in hand specimens. The volume of fossils within the marlstones increases at several thin levels corresponding to muddy calcarenites with wavy internal structure, and common shallow water bivalves (e.g. ostreids).

From 19.43 m to 21.78 m of the Paja Fm, between 20.99 and 23.35 m from the base of the section (Fig. 5–3), the calcilutite interbeds disappear and the sequence is dominated by 5–18 cm-thick homogenous marlstones, interbedded with less indurated beds which display even interlaminae of clay shale and marlstone, as well as levels of decimeter size micritic concretions. They appear grayish-brown (Fig. 5–2) due to weathering. In visual estimate, rocks at this interval contain less than 10% fossils, consisting of phosphatic fish fragments, fewer ammonite fragments, and inoceramid bivalves. None of the beds show bioturbation.

5.4.2 Isotope Stratigraphy, TOC and TIC Values

The studied section is marked by a sharp contrast in the distribution pattern of the TIC, TOC and $\delta^{13}\text{C}_{\text{org}}$ values between the upper 1.56 m of the Rosablanca Fm and the lower 7.3 m of the Paja Fm. The following is the description of the section based on the character of its stable carbon isotope signal (Fig. 5-5):

Figure 5-5 Lithology, total inorganic carbon (TIC) as weight % CaCO_3 ; total organic carbon (TOC); and stable carbon isotopes ($\delta^{13}\text{C}_{\text{org}}$) in the Curiti section. C7 refers to the stable carbon isotope stage defined by Menegatti et al., 1998. Lithology: M, mudstone; W, wackestone; P, packstone. Age: MB-LA, mid-Barremian to Lower Aptian.

The upper 1.35 m of the Rosablanca Fm show a general increase trend from a value of -24.5 to -21.87‰, punctuated by two negative peaks of -24.71‰ at 0.8 m, and -23.09‰ at 1.35 m.

The second negative peak is located just below the phosphatic bed (Fig. 5–4h) at the top of the unit (Co-09-6a, Fig. 5–4g). This interval of Rosablanca Fm is also characterized by a general tendency of decreasing carbonate contents from the bottom to the top of the described segment, and it consistently displays low organic matter contents (TIC, 31–93.8%; TOC, 0.04–1.4%).

The transitional segment between the Rosablanca and Paja formations, between 1.35 and 1.95 m from the base of the section (Fig. 5–5), is characterized by steady increase in the $\delta^{13}\text{C}_{\text{org}}$ values from -22.08 to -20.82‰. This interval begins with a 10 cm-thick black shale with the lowest carbonate content in the section (TIC, 0.09%; TOC, 3.5%; Fig. 5–4f). In general, the shales, marlstones and limestones in this segment display TIC values from 0.09 to 84.7%, and TOC values from 2.6 to 4.7%.

Between 1.95m and 8.9m from the base of the section (Fig. 5–5), the Paja Fm displays a series of $\delta^{13}\text{C}_{\text{org}}$ values that mostly vary between -22.66 and -20.47‰, which comprise five distinctive negative peaks at 3.3 m (-24.6‰), 4.6 m (-23.56‰), 5.9 m (-22.9‰), 6.86 m (-23.46‰) and 7.15 m (-22.5‰). Three of these negative peaks correspond to calcareous concretion levels (e.g. Fig. 5–4e). This interval consists of lithologies with variable TIC (TIC, 5.5–97.2 %) and generally high TOC values, with 57% of the samples yielding TOC > 2%. The highest TOC values occur between 3.8 and 4.9 m (TOC, 2.98–8.84%). Concretion samples in this interval display the highest TIC, but low TOC values (TIC > 88%; TOC, 0.17–0.7%). The upper 2.31 m of the interval seems to be more affected by weathering (Fig. 5–2), thus their TOC values should be taken as minimal values.

Table 5-1 Pyrolysis Results

Sample	Total Organic Carbon TOC (%)	Free Hydrocarbons S1 (mg HC / g rk)	Generatable Hydrocarbons S2 (mg HC / g rk)	Total Hydrocarbon Generation Potential S1+S2 (mg HC / g rk)	Hydrogen Enrichment Index HI (mg HC / gm TOC)	Generatable Carbon Dioxide S3 (mg CO2 / g rk)	Oxygen Enrichment Index OI (mg CO2 / g TOC)	Transformation Ratio "PI" (S1 / S1+S2)	Temp. of Peak S2 Tmax (°C)
CO-09-21*	1.82	0.09	0.09	0.18	5	0.5	27	0.5	414
CO-09-130	7.13	0.02	0.04	0.06	1	0.11	2	0.33	398
CO-09-18	1.71	0.02	0.06	0.08	4	0.08	5	0.25	402
CO-09-17C*	7.05	0.04	0.07	0.11	1	0.23	3	0.36	456
CO-09-17B*	3.91	0.02	0.04	0.06	1	0.18	5	0.33	404
CO-09-6A	0.73	0.02	0	0.02	0	0.24	33	1	*
CO-09-4	0.66	0	0.04	0.04	6	0.18	27	0	467

*Result non attainable

5.4.3 Pyrolysis Analyses

Rock-Eval pyrolysis results from the seven samples of the Curití section are shown in table 1. These results are characterized by low values of free hydrocarbons (S1, 0–0.09 mg HC/g rk), low generatable hydrocarbons (S2, 0–0.9 mg HC/g rk) and low generatable carbon dioxide (S3, 0.08–0.24 mg CO₂/g rk), as well as very low values of hydrogen enrichment index (HI, 1–6 mg HC/g TOC), and oxygen enrichment index (OI, 2–33 mg HC/g TOC). Tmax values obtained vary between 402°C and 467°C, and show an average of 423.5°C (n=6), including 2 samples indicative of overmaturation. The transformation ratio (PI=S1/S1+S2) shows values from 0 to 0.5.

5.4.4 Biochronology of the Curití Section

Ammonite specimens collected from the Curití section were mostly found atop the Rosablanca Fm within a 17-cm-thick phosphatic bed (boundary bed), and 2 m below that boundary bed. Other specimens were collected from the upper part of the studied section within the Paja Fm.

Ammonites collected in the Rosablanca Fm 2 m below the boundary bed (site DMA 2919) yielded an autochthonous association, which includes *Pulchellia* and *Pseudohaploceras*. Levels containing *Pulchellia* specimens are considered to characterize the middle Barremian according to the zonation of Bürgl (1956), or the upper Lower Barremian *Pulchellia galeata*-Zone of Patarroyo (2004).

The 17 cm-thick phosphatic boundary bed (CO-09-6b, Figs. 5–3, 5–4H, 5–5) contains phosphatized specimens of *Pulchellia*, *Gerhardtia*, *Toxancyloceras*, *Karsteniceras* and *Prodeshayesites*?. These taxa, except *Prodeshayesites*, can be considered as part of the middle and Upper Barremian (in the sense of Bürgl 1956; or part of the upper Lower Barremian *Pulchellia galeata*-Zone, and the lower Upper Barremian *Heinzia veleziensis*-Zone of Patarroyo 2004). The specimens of *Prodeshayesites* would indicate the lowest Aptian. Blau (1993) also

reported the presence of *Ancyloceras matheronianum*, *Ancyloceras vandenheckii*, *Heteroceras* sp. and *Subpulchellia* sp. within the boundary phosphatic bed.

The listed above phosphatized ammonite faunas suggest that the boundary bed between the Rosablanca and Paja formations is a condensed deposit involving part of the middle Barremian, the Upper Barremian and part of the Lower Aptian record in the section.

Ammonites were also found in the interbeds of hard micritic limestones, and black shales of the Paja Fm between meters 9 and 11.5 from the base of the section (Fig. 5–3). This interval yielded *Colchidites breistrofferi* Kakabadze & Thieuloy, 1991 (levels CO-11-30 top, CO-09-31, CO-09-42, DMA 2925); *Kutatissites* sp. cf. *K. creutzbergi* Kakabadze & Hoedemaeker (CO-09-41, DMA-2926), and *Kutatissites creutzbergi* Kakabadze & Hoedemaeker, 2004 (CO-09-42, DMA-2929).

In Colombia, beds containing *Colchidites breistrofferi* have been assigned to the top of the Upper Barremian (Kakabadze & Thieuloy 1991; Kakabadze & Hoedemaeker 1997; Hoedemaeker 2004; Patarroyo 2004, 2009), although these assignments in some cases had no reliable stratigraphic support or independent evidence other than the distribution of the genus outside northern South America. Species assigned to the genus *Colchidites* are known in Barremian series in Europe, the Caucasus, Africa, and South America (Wright *et al.* 1996), *Colchidites* faunas are not, however, abundant in Colombia; but our paleontological combined with the geochemical data from the Curití section would indicate that the range of *Colchidites* extended into the Early Aptian, as previously suggested by Kakabadze & Thieuloy (1991).

Kutatissites creutzbergi was described from Colombian material lacking careful stratigraphic control, and was attributed to the uppermost? Barremian by Kakabadze & Hoedemaeker (2004). The genus *Kutatissites* is known in Europe between the Upper Barremian (Sarasini Zone cf. Delanoy *et al.* 2000) and the Lower Aptian (Wright *et al.* 1996). *Kutatissites*

has also been reported in Colombia from middle Aptian *Dufrenoyia sanctorum*-*Stoyanowiceras treffryanus* Zone (Etayo-Serna 1983).

At 16.9 m above the base of the section (Fig. 5–3), a concretion level of the Paja Fm yielded *Epicheloniceras* sp. and *Riedelites obliquum* (Riedel, 1938), this assemblage has been reported in the Colombian Eastern Cordillera as part of the basal middle Aptian *Dufrenoyia sanctorum*-*Stoyanowiceras treffryanus* Zone (Etayo-Serna 1979).

An alternative biochronology would suggest a mid- Barremian age (late Early Barremian in the sense of Patarroyo 2004) for the phosphatic boundary level between Rosablanca and Paja formations, even though there is a recorded presence of *Ancyloceras matheronianum* and *Prodeshayesites* at this level. This suggestion would assume a terminal Barremian age for the levels of *Kutatissites* and *Colchidites* at meters 9 and 11.5, or 7.45 and 9.95 meters above the phosphatic bed. Such assumption is not only contrary to the paleontological evidence in Colombia (Etayo-Serna, 1983; Kakabadze & Thieuloy, 1991), but would imply an unlikely total thickness of 5 m for the whole Lower Aptian in the studied section.

5.5 Discussion

5.5.1 Paleoenvironments of the Curití Section

Low TOC and abundant, well-preserved articulated bivalve fauna, displaying fabrics of transport (imbrications, dense packing) in the 96-cm mid-Barremian (upper Lower Barremian *sensu* Patarroyo, 2004) basal interval of the Rosablanca Fm, are indicative of accumulation of bioclasts induced by storms in an otherwise low-energy, and well-oxygenated, subtidal environment (Figs 5–3, 5–5). The overlying interval, up to 1.39 m, of black, fossiliferous micrites/calcmudstones with scarce fish bones, echinoderm fragments, and phosphatic intraclasts, shows increasing influence of phosphate accumulation in a quiet subtidal environment (e.g. Fig. 5–4g). Absence of bioturbation, together with increasing OM content, and the scarcity of benthic fossils, indicates a change toward suboxic conditions. These results further corroborate

previous studies (Mann 1995) that reported increasing content of OM as carbonate content decreased throughout the interval. Our petrographic observations are also in agreement with increasing C/S ratios to values slightly above 2.8 observed by Mann (1995). The general increase in terrigenous quartz indicates a greater flux from the continent, and the C/N ratios (5–34) further indicate a mixed origin, marine and terrestrial, for the organic matter at the top interval of the Rosablanca Fm (Mann 1995).

The top 17 cm of the Rosablanca Fm that forms the boundary bed is most remarkable because it consists of calcareous and pyritic phosphorite (Fig. 5–4h) with middle and Upper Barremian, and Lower Aptian faunas (Fig. 5–3). This complex deposit involves phosphatization during condensation/non deposition, with periods of oxygenation that allowed recurrence of benthic faunas (e.g. lucinid bivalves), alternating with periods of anoxia in which biogenic particles originated essentially from nektonic communities. This phosphatic level also shows evidence of mechanical reworking as recorded by the irregular base of the bed, and presence of wavy lamination. Different degrees of alteration (bioerosion) of the skeletal components indicate accumulation of particles of different generations during long periods of time. Relatively low TOC values in this bed are also in agreement with oxidation of OM related to long periods of exposure close to the sediment/water interface.

The stable carbon isotope signal of the Rosablanca Fm's uppermost phosphatic level (6b) shows a continuously ascending series of values with the lowest 39 cm of the superjacent Paja Fm. Nonetheless, the presence of middle and Upper Barremian associated with the Lower Aptian ammonites in such phosphatic level, together with wavy lamination, indicate extensive winnowing and condensation during that period of time.

The studied 21.8 m interval of Paja Formation show sharp sedimentological contrast with the Rosablanca Fm. The lower 6.31m interval of the Paja Fm is dominated by organic-rich, black clay-shales, calcareous clay-shales and marlstones. Rocks at this interval lack bioturbation, and

shows well-preserved, even lamination. It includes high TOC (up to 8.8%) and dispersive framboidal pyrite, very rare benthic fossils, and the significant increase in the C/S ratios (up to 64.1 cf. Mann, 1995). These beds were deposited in a quiet environment with high supply of terrigenous components including 10–15% of quartz, and OM with high C/N ratios (5–182); Mann (1995). The record shows evidence of the dominance of oxygen-depleted conditions, and increased productivity related to high supply of nutrients from the mainland. Black calcilutite interbeds display lower TOC, C/N, and C/S values indicating higher components of marine origin, and less severe anoxia/dysoxia than the shales (Mann 1995).

The frequency of the calcilutite beds in the section increases between 6.31 and 14.94 m of the Paja Fm (between 7.87 and 16.5 m from the base of the section). Black marlstones, calcareous clay-shales and calcilutites display similar facies to those of the lower part of the formation, in which high preservation of lamination, absence of bioturbation and scarcity of fossils (calcspheres, fish scales/bones, inoceramids) indicate persistent anoxic or suboxic conditions. Some biocalcilutite interbeds and concretions include pellets, ostracods, juvenile molluscs, in addition to fish scales and bones, suggesting rather oxic conditions. Minor interbeds of phosphatic fossiliferous marlstones display evidence of mechanically concentrated calcareous and phosphatic allochems including fish bones, intraclasts and shallow water bivalves associated with ripples, imbrication and irregular surfaces.

Between 14.94 m and 19.43 m of the Paja Formation, in the Upper Aptian portion of the unit (16.5 to 21 m above the base of the studied section), there is an increase in the frequency of the interbeds with marlstones, calcarenites and biocalcarenites with of mechanically concentrated shallow water mollusks. The frequency of such fossiliferous levels interbedded with well-laminated black shales, black marlstones and calcilutites indicate an increase in fluctuating dynamic conditions at an otherwise anoxic to suboxic sediment-water interface.

In summary, the Rosablanca Fm at Curití shows a record of sea level rise during the middle Barremian with gradual depletion in oxygen conditions in the basin. These changes in environmental conditions observed in the petrographic and geochemical data are in agreement with previous studies that reported change in the microfacies, as well as changes in the content and character of the OM (Blau 1993; Mann 1995). A period of condensation during the middle Barremian-Lower Aptian led to accumulation of a phosphatic bed and low preservation of OM. The studied interval of the Paja Fm indicates deeper shelf environments marked by periods with higher supply of terrigenous minerals (clay, quartz). Concomitant increases in OM suggest that nutrient supply from the mainland was at the beginning of enhanced productivity in the basin that led to deposit of black shales in a poorly oxygenated environment. The state of an oxygen-deficient bottom persisted into the middle Aptian portion of the section, although the beginning of the middle Aptian coincides with a remarkable increase in the influx of bioclastic materials from shallower areas into deeper parts of the basin.

5.5.2 Stable Carbon Isotope Stratigraphy at the Curití Section and the Timing for Anoxia

The uppermost part of the Rosablanca Fm (from 0 to 1.35 m) in the studied section displays a trend of increasing carbon isotope values between -24.5 and -21.87‰, punctuated by two negative peaks of -24.71‰ and -23.09‰. Similarly, stable carbon isotope records on carbonates from expanded Barremian sections (e.g. Angles, SE France, Godet *et al.* 2006) include a negative peak in the transition between the Tethyan upper Lower Barremian *Compressisima* and *Darsi* ammonite biozones. However, correlation with the more pronounced negative peak observed in the Rosablanca Fm series is uncertain because of the limited amount of data available, and the correlation between middle/Upper Barremian biozones between Colombia and the Mediterranean region is not well defined.

Figure 5-6 Correlation of stable carbon isotope curves between the Curití section (Colombia), and sections in SE France (Vocontian basin), NE Mexico (Santa Rosa Canyon) and the southern Italian Alps (Cismon). C1 to C8 refer to the stable carbon isotope stages defined by Menegatti *et al.* (1998). C9 to C13 refer to the stable carbon isotope stages introduced by Bralower *et al.* (1999). Ap6 to Ap15 and A11 to A16 correspond to isotope stages used by Herrle *et al.* (2004). We use here the geochemical definition of Oceanic Anoxic Event 1a (OAE-1a) ranging between isotope stages C3 and C6, independently of the presence or absence of organic-rich sediments. Note that the geochemical signature of OAE-1a is absent in the studied section at Curití, Colombia, due to a hiatus affecting part of the Lower Aptian.

Immediately above the Rosablanca Formation, the lowermost 0.6 m of the Paja Formation, between 1.35 and 1.95 m above the base of the section, is characterized by steady increases in the $\delta^{13}\text{C}_{\text{org}}$ values from -22.08 to -20.82‰. This trend in the stable carbon isotope values occurs above a small negative peak in level 6a (Fig. 5-4g, 5-5), and includes the phosphatic boundary bed (Figs. 5-4h, 5-5) of the Rosablanca Fm characterized by a mixed middle and Upper Barremian, and Lower Aptian ammonites (Fig. 5-3).

Figure 5-7 Correlation of stable carbon isotope curves between the Curití section (Colombia), and sections in the Prebetic and Subbetic ranges of Spain (Cau, Raco Ample and La Frontera), and Sicily (Calabianca). C1 to C8 refer to the stable carbon isotope stages defined by Menegatti *et al.* (1998). We use here the geochemical definition of Oceanic Anoxic Event 1a (OAE-1a) ranging between isotope stages C3 and C6, independent of the presence or absence of organic-rich sediments. Note that the geochemical signature of OAE-1a is absent in the studied section at Curití, Colombia, due to a hiatus affecting part of the Lower Aptian.

This bed is interpreted as a level with stratigraphic condensation. The $\delta^{13}\text{C}_{\text{org}}$ values, between 1.95 m and 8.9 m above the base of the section, display relatively low variability of highly positive values between -22.66 and -20.47‰. That interval did not yield ammonites, but taxa such as *Epicheloniceras* sp. and *Riedelites obliquum*, occurred further up in the sequence at 15.3 m. These taxa are common in the local biozone of *Dufrenoyia sanctorum-Stoyanowiceras treffryanus* Zone (Etayo-Serna 1979), representative of the base of the middle Aptian (Upper Aptian in Etayo-Serna, 1979). Available stable carbon isotope records of carbonate and organic matter for Aptian sections in the Vocontian basin, the Alps and Mexico (Menegatti *et al.* 1998; Bralower *et al.* 1999; Herrle *et al.* 2004), show three intervals of high $\delta^{13}\text{C}$ values in the Lower Aptian (C5 stage), Lower/ middle Aptian transition (C7 stage), and uppermost Aptian (C10 stage). Of these three intervals of high $\delta^{13}\text{C}$ values, C7 reached the maximum in the Aptian, and is most comparable in age, pattern and magnitude to the data obtained in the basal 7.35 m interval of the Paja Fm at the Curití section. However, $\delta^{13}\text{C}_{\text{org}}$ values during interval C7 at Curití appears higher (up to ~3.3‰) than those reported for the same interval by authors such as Menegatti *et al.* (1998), Bralower *et al.* (1999), Gea *et al.* (2003), Wortmann *et al.* (2004). These high $\delta^{13}\text{C}_{\text{org}}$ values observed at Curití are consistent, despite the presence of organic matter of terrestrial origin in the bulk component, as suggested by C/N ratios (Mann 1995) ranging between 5 and 182.

As presented in the biostratigraphy and biochronology descriptions above, the presence of *Kutatissites* and *Colchidites*, in the lower part of Paja Fm may arguably be indicative of the top of the Barremian in the section. Such assumption would dismiss the paleontological evidence (Etayo-Serna, 1983; Kakabadze and Thieuloy, 1991), as well as for the presence of lower Aptian taxa (*Prodeshayesites*) found within the phosphatic boundary bed. Likewise, such interpretation would imply an Upper Barremian position for the basal, black, shale-rich interval of Paja Fm, between 1.56 and 9 m of the section. In such a case, its carbon isotope excursion has a potential correlation with the interval of high positive carbon isotope values associated with the *Giraudi*

Zone (stage B7 of Wissler *et al.*, 2003). However, the isotope values ($\delta^{13}\text{C}_{\text{carb}}$) within the *Giraudi* Zone yield amounts in the order of 1 to 2‰ lower than those reported for the Aptian isotopic stage C7 (Erba *et al.* 1999; Wissler *et al.* 2003; Bodin *et al.* 2006; Föllmi *et al.* 2006). Our carbon isotope values in organic matter obtained from the lower interval of the Paja Fm are on average 3.3 ‰ higher than those reported for the C7 interval in the literature, therefore it cannot be mistakenly confused with the weak $\delta^{13}\text{C}$ Barremian signal. In fact, C7 is characteristically distinct because it includes the highest carbon isotope ($\delta^{13}\text{C}_{\text{org}}$, $\delta^{13}\text{C}_{\text{carb}}$) values recorded throughout the Lower Cretaceous series, even higher than the time interval that includes OAE1a.

A possible explanation for the very high $\delta^{13}\text{C}_{\text{org}}$ in the Paja Fm is manifested in their degree of thermal maturation. Indeed, pyrolysis analyses performed on seven selected samples of Paja Fm at Curití resulted in T_{max} between 398 and 467°C, as well as very low values of Hydrogen (HI) and Oxygen Index (OI) that suggest a history of high thermal maturation of the kerogen (Whelan & Thompson-Rizer 1993; Dembicki 2009). Thermal maturation of kerogen types II and III is known to increase the $\delta^{13}\text{C}$ values up to 4 ‰ (Whelan & Thompson-Rizer 1993; Dembicki 2009).

In summary, the absence of isotopic segments C3, C4, C5 and C6?, suggests that OAE-1a is missing in the studied Curití section of the Paja Fm. These results also suggest that the ascending isotopic values between 1.56 and 1.95 m above the base of the section, may be assigned to either isotopic stages C6 or C7, and are more compatible with C7. Thus, the phosphatic bed at the top of the Rosablanca Fm (bed Co-09-6b) characterized by the accumulation of a phosphatized assemblage of middle Barremian, Upper Barremian and Lower Aptian ammonites forming a complex condensed bed, would include the time interval corresponding to OAE-1a. The carbon isotopic signal in the interval of the Paja Fm between 1.56 and 9 m at Curití suggest that the organic-rich shales accumulated under prevailing oxygen-defficient conditions coincident with isotopic stage C7. The values obtained at Curití are in

agreement with isotope values reflecting a worldwide response to changes in the ocean carbon reservoir at that time, and subsequent to the global level of anoxia known as OAE-1a.

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6 SEDIMENTOLOGICAL AND GEOCHEMICAL EVIDENCE FOR PALEOENVIRONMENTAL CHANGES COEVAL WITH OCEANIC ANOXIC EVENT 1A (OAE-1A) IN THE LOWER APTIAN SECTION OF MADOTZ (BASQUE CANTABRIAN BASIN, SPAIN)

Abstract

A 62.5 m Lower Aptian sequence near Madotz (Navarra, Spain), comprises carbonate and mixed carbonate-terrigenous deposits that clearly document successions of paleoenvironments prior to, during and subsequent to OAE-1a. The study integrated multiple proxies, including fossil assemblages, microfacies, XRD bulk and clay mineralogy, inorganic (major, minor, trace elements redox indicators), and organic geochemistry (Rock-Eval pyrolysis and biomarker analysis), combined with previously published results (TOC, TIC and $\delta^{13}\text{C}_{\text{org}}$). The lowest Unit 1 (0–3 m) accounts for a well-oxygenated, low-energy, siliciclastic-dominated environment prior to OAE-1a. Subunit 2a (3–23 m) contains highly diverse Urgonian-type assemblages, rich in phototrophic organisms (photozoan assemblages), and is essentially a carbonate platform margin deposit developed in an oligotrophic environment, between the fair-weather and storm wave bases. Subunit 2b (23–47.4 m) is the most significant portion of the section as it coincides with a major switch to mixed carbonate-terrigenous deposits that characterize major environmental changes concomitant with the onset and development of conditions associated with the interval corresponding to OAE-1a (C4–C6 $\delta^{13}\text{C}$ stages). Subunit 2b reveals a general increase in the percentage of clay minerals, increase in the kaolinite/smectite ratio, changes to low diversity heterozoan assemblages dominated either by orbitolinids or other agglutinated foraminifera, and a shale level lacking or containing rare benthic foraminifers. The interval of subunit 2b between 26.6 and 36 m, which correlates with OAE-1a stable carbon isotope stages C4 and most of C5, is here interpreted as a transgressive system (TST). Pyritic clay-shales with low bioturbation index and enriched in organic matter are concurrent with the maximal flooding surface (MFS, ~36 m) and the beginning of the highstand system tract (HST). These shales have the highest content of

clays, and the peaks of Al, Si, K, Fe, Mg and Ti. They also show even lamination, rare fossil content and pristane/phytane ratio 0.88. Relatively low values of Mn/Al are consistent with oxygen-depleted bottom waters and Gammacerane content suggests water-column stratification. Most of the clay-rich levels, however, accumulated under fully or intermittently oxygenated water column, resulting in no enrichment in organic matter or the redox sensitive trace elements, although reducing conditions and pyrite formation developed in the pore waters. The sedimentological and geochemical changes during C4 and C5 coincide with a time of climatic shift toward a more humid regime, coupled with transgression, and increased input in nutrients indicated by the clay assemblages and the total P values. Organic matter within this level reveals both terrigenous and marine inputs as indicated by the biomarkers.

The highstand system tract (HST) includes the upper part of subunit 2b, coeval with the terminal part of isotope stage C5; it continues into subunit 2c, corresponding to stage C7. Orbitolinid-rich shoals were dominant during C6, while lagoonal and rudist-dominated inner platform carbonates were typical of C7 stage. The HST thus displays the slow recovery of carbonate sedimentation with progress toward drier climate as shown by the reduction of clay content and the character of the clay assemblages richer in smectite.

6.1 Introduction

The Mid-Cretaceous greenhouse climate is associated with the Early Aptian (~120 Ma) pronounced environmental and global carbon cycle perturbations known as Oceanic Anoxic Event 1a (OAE-1a), with duration between 1.0 and 1.3 Ma (Li et al., 2008). The OAE-1a interval shows a record of enhanced accumulation of organic-carbon-rich sediments in pelagic and hemipelagic environments (Menegatti et al., 1998; Bellanca et al., 2002; de Gea et al., 2003; Dumitrescu and Brassell, 2005; Luciani et al., 2006; Rückheim et al., 2006).

Among the different factors discussed in the literature that may have led to such conditions, high productivity coupled with increases in water temperatures, paleogeographic

restrictions, and fresh water fluxes, are all conceivable contributors that can significantly enhance stratification in the water column, hence diminishing the resupply of oxygen to marine subsurface waters. The interplay of the different factors that led to OAE-1a is still uncertain. Generally, Early Aptian increased temperatures (Menegatti et al., 1998; Bellanca et al., 2002; Dumitrescu et al., 2006; Luciani et al., 2006; Sprovieri et al., 2006; Ando et al., 2008; Stein et al., 2011) have been related to massive injections of CO₂ by Pacific volcanism (Larson and Erba, 1999; Weissert and Erba, 2004; Méhay et al., 2009; Tejada et al., 2009; Bottini et al., 2012), as well as the release of methane hydrates (Méhay et al., 2009). Global temperature increase is argued to have induced gentler latitudinal gradient (Clarke and Jenkyns, 1999) that caused weaker ocean circulation, which had a negative impact on the water ability to dissolve and retain gases. Furthermore, increased input of nutrients into the oceans related to increased weathering rates on the continent (Tejada et al., 2009; Bottini et al., 2012) and accrued deep sea hydrothermal activity led to high local/global primary productivity (Erba and Tremolada, 2004; Dumitrescu and Brassell, 2005; de Gea et al., 2008; Heldt et al., 2008; Erba et al., 2010) enhanced the vertical expansion of the oxygen minimum zone bringing anoxia to shelves and platform margins (Schlanger and Jenkyns, 1976) particularly during sea level rise.

At the time of OAE-1a, sedimentological, paleontological and geochemical evidence support increased flux of nutrient and/or increased primary productivity in mixed shallow water terrigenous/carbonate and carbonate settings (Pittet et al., 2002; Immenhauser et al., 2005; Huck et al., 2010; Rameil et al., 2010), as well as in hemipelagic and pelagic environments (Erba and Tremolada, 2004; Dumitrescu and Brassell, 2005; Luciani et al., 2006; Heldt et al., 2008). This is confirmed by a synchronous major negative excursion of marine ¹⁸⁷Os/¹⁸⁸Os (Tejada et al., 2009; Bottini et al., 2012) indicative of increased supply of non-radiogenic Os by weathering from continents. Recent sedimentological and microfacies studies of OAE-1a equivalents in shallow-water settings (Immenhauser et al., 2005; Burla et al., 2008; Millán et al., 2009; Embry et al.,

2010; Huck et al., 2010; Bover-Arnal et al., 2011; Najarro et al., 2011), show that carbonate production around that interval can be permanently or temporarily replaced by terrigenous sediments with episodic development of abundant orbitolinid faunas (Wissler et al., 2003; Luciani et al., 2004; Föllmi and Gainon, 2008; Masse et al., 2009). In other cases these environments develop microbial carbonates such as those reported in Oman (Pittet et al., 2002; Immenhauser et al., 2005; Rameil et al., 2010), and in the Adriatic region (Huck et al., 2010). Such environmental changes are generally attributed to a fluctuating nutrient regime controlled by paleoclimate

The Madotz section exemplifies the temporal interruption of the carbonate urgonian-type facies during OAE-1a when mixed carbonate/terrigenous deposits took over with frequent accumulations of orbitolinids and smaller development of organic-rich shales (Gaona-Narvaez et al., 2009; Gaona-Narvaez et al., 2013). The aim of the present work is to provide detailed sedimentological and geochemical evidence to further our understanding of the main contributing local paleoenvironmental factors that triggered oxygen depletion at that location. The study used a multiproxy approach that integrates microfacies analyses, SEM/EDS petrographic observations, XRD bulk and specific clay mineral data, Rock-Eval pyrolysis, biomarkers analyses, and elemental analyses (major, minor, trace elements). These results have been complemented with previously published data that include total inorganic carbon (TIC, weight % CaCO_3), total organic carbon (TOC, weight %C), and stable carbon isotope results (Gaona-Narvaez et al., 2013).

6.2 Geographic and Geologic Setting

The Madotz section is located immediately northwest of the town of Madotz (sheet #114 Alsasua 1:50000: long. 42°56'24", lat. 1°52'30"), in the southeastern portion of the "Sierra de Aralar", close to the boundaries between the provinces of Guipuzcoa (Basque country) and Navarra (Figure 6-1). The lithology of the Sierra de Aralar is discussed in Gaona et al (2012), it shows an environmental evolution from deltaic conditions in the latest Jurassic to widespread

Figure 6-1 Location of the studied section at Madotz. Geological contacts after Duvernois et al. (1972).

open marine organic-rich limestones and mudrocks in the Barremian. The extensive limestone deposits that started in the Aralar in the Early Aptian continued into Albian. They are characteristically rich in rudists (Urgonian facies), and intermittently interrupted by intervals of orbitolinid-rich marlstones, mudrocks and shales. These carbonate platform deposits developed concurrently with the transition from initial rifting to spreading in the adjacent Bay of Biscay (García-Mondéjar et al., 1996).

The Aptian stage in the Madotz area includes five informal stratigraphic units (Duvernois et al., (1972), Figure 6-1, with a first biochronology based on benthic foraminifera (Cherchi and Schroeder, 1998), subsequently amended based on ammonites (García-Mondéjar et al., 2009; Gaona-Narvaez et al., 2013). Hence, the present study follows the biochronology published by Gaona-Narvaez et al. (2013), Figure 6-2, and the informal rock units established by Duvernois et al. (1972). The study focuses on the basal 62.5m of the Lower Aptian section known as “Madotz Limestone” (“Ensemble II” in Duvernois et al., 1972; =Unit 2 in Cherchi and Schroeder, 1998).

The “Madotz Limestone” includes in ascending order (Figure 6-1, **Error! Reference source not found.**): subunit 2a (coral-algae-bivalve rich limestone), subunit 2b (orbitolinid-rich

marls), and subunit 2c (rudistid- rich limestone). Based on the carbon isotope signal in organic matter Gaona-Narvaez, et al. (2013) concluded that subunit 2b spans $\delta^{13}\text{C}_{\text{org}}$ stages C4 to C6 (Menegatti et al, 1998), and is equivalent to the time interval of OAE-1a.

Figure 6-2 Stratigraphy of the Aptian sequence at Madotz. Chrono and magnetostratigraphy from Ogg and Ogg (2008), ammonite biozones from Reboulet et al. (2012). Lithostratigraphy and orbitolinid biochronology modified from Cherchi and Schroeder (1998).

6.3 Materials and Methods

This study includes a high-resolution sampling of 62.5 m of the Madotz section (outcrop and trenches), from the top of unit 1 (3 m), units 2a (20 m) and 2b (24.4 m), to the basal 15 m of subunit 2c of the “Madotz Limestone” (**Error! Reference source not found., Error! Reference source not found.**). Inorganic and organic carbon contents are based on previous work, as well as

the lithologic terms, limestone, marlstone, calcareous mudrocks and mudrocks, (Gaona-Narvaez et al, 2013); Figure 6-12.

6.3.1 Microfacies Study

Initial petrographic and microfacies analyses were carried out on a total of 86 samples. The analyses involved conventional transmitted light microscopy on all the samples, and scanning electron microscopy on selected samples; SEM analyses was conducted with a JEOL JSM 5910LV available at the Florida Center for analytical Electron Microscopy (FCAEM). Both at the field scale and microscopic scale special attention was given to the presence/absence of benthic fauna, bioturbation and early diagenetic minerals indicative of redox conditions.

6.3.2 Pyrolysis

Pyrolysis on bulk samples was performed on seven samples representative of all fine-grained lithologic types present in subunit 2b, using a ROCK-EVAL II-PLUS analyzer (Vinci Technologies) in the Center of Petroleum Geochemistry at the University of Houston. Whole rock powdered samples (50 to 100 mg) are weighed accurately into metal crucibles that, and then placed on the auto-sampler tray, and conveyed sequentially into a furnace initially maintained isothermally at 300°C. Free hydrocarbons are volatilized and quantified by the instrument's flame ionization detector (FID) to give Peak 1 ("S1" in mg hydrocarbons/g rock, free hydrocarbons). The furnace temperature is then automatically increased to 550°C at 25°C per minute. Within this temperature range, kerogen will crack to give hydrocarbons, which are also measured by the FID to give Peak 2 ("S2" in mg hydrocarbons/g rock, generatable hydrocarbons), and carbon dioxide, measured by a thermal conductivity detector (TCD) within the instrument to give Peak 3 ("S3" in mg CO₂/g rock, generatable carbon dioxide). The temperature at the maximum rate of evolution of cracked volatiles is given by (T_{max}). In order to evaluate the maturity and kerogen type, the following parameters are also obtained: hydrogen enrichment index ($HI=S2/TOC*100$), oxygen enrichment index ($OI=S3/TOC*100$), and the transformation ratio ($PI=S1/S1+S2$).

6.3.3 Bulk and Clay Mineralogy

Semi-quantitative bulk mineral and specific clay mineral analyses were performed by X-ray diffraction (XRD) methods on 17 and 15 samples, respectively, collected in unit 1, subunits 2a, 2b, and the base of 2c. The analyses were performed in the Industrial Minerals Section of the Illinois State Geological Survey (ISGS, Champaign, IL) on a Scintag XDS 2000 diffractometer; the Jade+R software (Materials Data Inc.) was used for semiquantitative data assessment. For the analysis of bulk-mineral content, 2 g of sample were initially micronized with DI water in a McCroneR micronizing mill and centrifuged. After separation of the supernatant, the remaining sample was dried overnight, homogenized, and packed into an end-loading sample holder as a random powder bulk-pack to be analyzed in the diffractometer. Step-scanned data were collected from 2° to 60° 2 θ with a fixed time of 5 seconds per 0.05° 2 θ for each sample.

Analyses of samples for XRD clay mineralogy use oriented mounts of clay-sized particles (<2 μm). Sample preparation is based on Moore & Reynolds (1997) and Goetsch et al., (2012). Clay mineral content was calculated after two treatments (overnight air drying and treatment with ethylene glycol for 24h), to display the change in spectra by comparing peak height ratios among expandable clays (smectite or mixed layer smectite), illite, kaolinite, and chlorite. Air-dried and glycolated samples were step-scanned from 2° to 34° 2 θ with a fixed time of 5 seconds per 0.05° 2 θ for each sample for each sample. Estimates were produced in relation to the area based on Moore & Reynolds (1997).

6.3.4 Biomarkers

The *n*-alkanes, acyclic isoprenoids, saturated and aromatic biomarkers identification of rock extracts was conducted on a single sample (ES-08-46B) collected at 36.8 m from the base of the measured section. Bitumen extraction, chromatographic separation, gas chromatography and mass spectrometry (GC, GC-MS), was carried out by Weatherford Laboratories (Shenandoah, TX). Soluble bitumen from the powdered sample was extracted with dichloromethane using a

Soxhlet apparatus. Medium pressure liquid chromatography (MPLC) was used to isolate the saturated and aromatic fractions. After separation, rock extract was analyzed for fingerprints with an HP6890 gas chromatograph. Biomarkers were identified on both the saturated and aromatic hydrocarbon fractions using gas chromatography-mass spectrometry (GC-MS), with an HP6890 gas chromatograph, equipped with an on-column injector, coupled to a HP5973 mass-selective detector (MSD).

The saturated biomarkers were separated using a DB-5 column (60 m * 0.25 mm * 0.25 μ m film thickness), and the following temperature program: from 100°C (0 min) to 170 °C at 20°C/min, then to 290°C at 1.5°C /min, and finally to 320°C at 2°C /min (hold 20 min). The carrier gas was He at constant flow (0.8 mL/min). The MSD instrument was operated in selected ion monitoring mode (SIM, 0.95 cycles/sec). Ions were collected in two time windows extending from 5 to 30 minutes and from 30 to 118.5 minutes

The aromatic fraction, the GC-MS was separated on a DB-1 column (60 m * 0.25 mm * 0.1 μ m film thickness) using a temperature program from 70°C (3 min) to 150°C at 1.5°C /min, and to 315°C at 3°C /min (hold 20 min). The MSD was operated on selected ion monitoring mode (SIM, 0.98 cycles/sec). The carrier gas was He at constant flow (0.9 mL/min). Ions were collected in two time windows extending from 5 to 77.8 min, and from 77.8 to 131.33 min. For both aromatic and saturated compounds, in all windows the dwell time was set to 20 ms for each ion.

6.3.5 Elemental Analyses

Nineteen samples of subunit 2b were analyzed for elemental components using a LA-ICP-MS at the Trace Evidence Analysis Facility (TEAF) at Florida International University. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is a reliable technique that allows simultaneous determination of major, minor and trace elements on samples of soil and sediment with limits of detection as low as 0.01 mg/kg (Arroyo et al., 2009). The

technique uses pressed sediment pellets spiked with scandium oxide in a concentration of 1000 ppm in 3% acid solution as internal standard. The pellets were ablated in a CETAC LSX-500 with a 200 μm spot size, at 10Hz of frequency and 3.01mJ of energy during 60 sec. Four replicates were obtained in each pellet from which the average is reported. Only values with relative standard deviation below 20% were included in the interpretation. The micro-droplets generated by interaction between the laser and the particles were analyzed in an ELAN-DRCII – ICP-MS (Perkins) using He as a carrier gas. Data were processed with GLITTER software (GEMOC, Macquarie University, Australia) or with GEOPRO software (1999, v 1.0, CETAC, USA). The following standards were used: the sediment reference material PACS-2 (National Research Council of Canada); and the soil reference materials, SRM NIST 2710 (Montana Soil) and NIST 2704 (US Department of Commerce, National Institute of Standards and Technology).

6.4 Results

6.4.1 Lithology and Fossils

The Lower Aptian Stage at Madotz (Units 1 and 2, Duvernois et al., 1972; Cherchi and Schroeder, 1998) reveals significant temporal variations within the sequence that comprises an early stage of terrigenous deposits (Unit 1), followed by Urgonian-type limestones (Unit 2a), interbeds of mudrocks and orbitolinid-rich marlstones (Unit 2b), and a late stage of Urgonian limestones (Unit 2c).

Unit 1 (0–3 m; Figs. 6–3) consists of bioturbated medium gray to olive gray (N5, 5Y 4/1) claystones. At the field scale the fossil association reveals rare, whole or fragmented shells of endobenthic bivalves (tellinoids, nukuloids, arcoids), gastropods (Aporrhaidae), ammonites (*Deshayesites* cf. *forbesi* Casey and *Pseudohaploceras*? sp.), decapods, wood fragments, and burrows 3-5 mm in diameter. This unit is further described below as Microfacies M1 (Figure 6-5A).

Figure 6-3 Lithologic log of the studied interval of the Madotz section.

Figure 6-4 Studied outcrops of the “Madotz Limestone”, including subunits 2b, the lower part of subunit 2c, a 1.8m thick shale bed characterizes microfacies M7 and M8 from 36 to 37.8m. Note interval dominated by orbitolinid-rich biocalcirudites (*Orb bcr*) (6-3A). Outcrops of the orbitolinid biocalcirudite (*Orb bcr*) characterizes microfacies M4 and M5, in the upper part of subunit 2b, and the limestones at the base of subunit 2c (6-3B).

Unit 2 comprises subunit 2a (3–23 m), 2b (23–47.4 m), and 2c respectively:

Subunit 2a is 20 meters thick and shows subtle temporal variation at the field scale:

The basal part, from 3 m to 5.6 m (Figs. 6-3, 6-4A) shows a transition from the underlying terrigenous facies to predominately carbonate Urganian facies. This interval is poorly exposed and consists of 20–30 cm-thick tabular beds of limestones which in hand specimens show three types of fossil assemblages: medium dark gray (N4) biocalcarenites with bivalves and benthic foraminifers; dark gray (N3) biocalcarenites with corals and bivalves; and olive gray (5Y 4/1) biocalcirudites with bivalves and orbitolinids, which are described as microfacies M2, M3, and M4, respectively (Figure 6-5). Subunit 2a continues from 5.6 to 23 m or over a thickness of 17.4 meters (Figs. 6-3, 6-4a), and consists of medium light gray, light olive gray and yellowish gray (N6, 5Y 6/1, 5Y 8/1) nodular, highly recrystallized biocalcarenites and biocalcirudites (10–170 cm thick), which display wavy-bedding. This interval can be further differentiated based on observed macroscopic differences in fossil assemblages and texture:

From 5.6 to 13.2 m the texture is grain-supported, and the assemblage is rich in coral and bivalve fragments. This interval is also equivalent to Microfacies M3 (Figure 6-5d-f). From 13.2 to 16.5 m this interval also includes coral fragments, but they are relatively less abundant than other unidentifiable bioclasts. In hand samples the texture is strongly recrystallized and will be also described microscopically as microfacies M3. From 16.5 m to 17.4 m an important change is observed where Subunit 2a displays gray nodular texture of grain-supported biocalcarenite (e.g. level ES-06-14, Figure 6-5h) that contain articulated bivalves, and sudden recurrence of scarce orbitolinids. This lithology is similar to Microfacies M4. The uppermost part of subunit 2a from 18 to 23 m consists also of grain-supported calcirudites with bivalves, and common corals, which are easily identified in hand specimen. This lithology is described as Microfacies M3.

Subunit 2b comprises 24.4 meters of varying lithologies. From 23 to 26.6 m the outcrop was buried under slope wash in a subsequent valley, but we integrate this interval in the basal part of subunit 2b because the valley is indicative of a lithology softer than the infrajacent hard

limestone of subunit 2a. The exposed lower part of subunit 2b (26.6 to 42.3 m; Figs. 6–3, 6–4A) consists in general of 15 to 210 cm-thick interbeds of indurated marly limestones (muddy biocalcirudite and biocalcilutite, bioclastic marlstone), and less indurated interbeds of marlstone, claystone and shale. This part of the section includes different lithologic packets that can be described as follows:

From 26.6 to 28.6 m the beds vary in thickness from 28 to 130 cm, are medium dark gray to olive gray (N4, 5Y 4/1) with wavy primary structures, and consist of grain-supported fine and medium biocalcirudite (size up to 5 mm diameter), as well as planar beds of matrix-supported bioclastic marlstone and claystone. These beds also show bioturbation, and a typical fossil assemblage dominated by *Palorbitolina lenticularis*, minor bivalves, echinoderms and brachiopods. These lithologies correspond to Microfacies M5.

From 28.6 to 32.3 m medium dark gray and dark gray (N4, N3) tabular beds of claystone and biocalcilutite (28–107 cm-thick) predominate. They contain scarce fossils (bivalves, echinoderms, brachiopods, orbitolinids), bioturbation is locally low, and occasionally pyrite occurs randomly scattered throughout with punctual development of nodules. These lithologies correspond to Microfacies M6 and M7 (Figures 6–3, 6–9). The interval also includes interbeds of biocalcirudite and bioclastic marlstone (20 to 23 cm thick) rich in *Palorbitolina lenticularis*, (Microfacies M5, Fig. 6–3, 6–6a, 6–9).

From 32.3 to 36 m, the lithology consists of medium dark gray (N4) bioturbated planar beds (10 to 110 cm thick) of biocalcilutite, marlstone and claystone. They typically contain scarce bivalves, echinoderms, orbitolinids, and ammonites (*Pseudosaynella bicurvata* (Michelin), *Pseudosaynella undulada* (Sarsin) and *Deshayesites cf. forbesi* Casey) that occur in the claystone beds. These beds are described as Microfacies M6 (Fig. 6–3, 6–9). Pyritic, bioturbated claystones with rare fossils occur locally, and are included in Microfacies M7. Beds of muddy

biocalcirudite and fossiliferous claystone dominated by *Palorbitolina lenticularis* (equivalent to Microfacies M5) toward the upper part of the interval.

From 36 to 37.8 m, the interval consists of remarkable dark gray to grayish black (N3, N2) claystone and clay-shale beds with dispersive pyrite, and relatively enriched in organic matter. The bulk of the 1.8-meter interval (Fig 6–2, 6–3) shows no apparent bioturbation and fossils, but apparent lamination occurs in the middle of the bed. Also, the base and topmost contacts (~25 cm thick) show faint burrows and rare fragments of shallow-water bivalve taxa, such as arcoids, cardiids, pholadomyoids, *Neithea* sp., echinoderms and ammonites (*Deshayesites* cf. *forbesi* Casey, *Deshayesites* sp.). These beds are assigned to Microfacies M7 and M8 (Figs. 6–6d–h, 6–7a–h, 6–8a–b, 6–9).

From 37.8 to 42.3 m there is recurrence of thick beds (20–210 cm thick) of grain-supported fine biocalcirudites, and matrix-supported bioclastic marlstones, and marlstones with the typical assemblage dominated by *Palorbitolina lenticularis*, identical to Microfacies M5 (Figs 6–3, 6–9). The uppermost part of subunit 2b (43.3–47.4 m; Figs. 6–3, 6–4b), shows another facies change. It is dominated by bedsets, 60 to 180 cm thick, with apparent wavy contacts, and are medium gray and medium dark gray (N5, N4). They consist of grain-supported, matrix-supported biocalcirudite, and calcarenite dominated by *Palorbitolina lenticularis*, including both conical and discoidal morphotypes. These beds also contain rare fragments of non rudist bivalves, brachiopods and echinoderms. This lithofacies and fossil association is a recurrence of the lithology associated with Microfacies M4 found at intervals 3–5.6 m, and 15.6–17.4 m, respectively (Figure 6–9).

Subunit 2c forms a prominent ledge known as Madotz Bar. The lowest part of subunit 2c (47.4–52.9 m; Figs. 6–3, 6–4B) consists of 15 to 80 cm-thick beds of medium gray and medium dark gray (N5, N4), calcilutite with scarce coarse bioclasts. Primary structures appear as parallel wavy bedding, and locally large-scale cross bedding. Fossil assemblages contain scattered

bivalves and corals, but orbitolinids are common only at the base of the interval. This interval is typical of Microfacies M9 (Figures 6–8c–d).

The uppermost part of the studied section (52.9–62.5 m; Figs. 6–3, 6–4b) represents only the lower portion of sub-unit 2c discussed in Duvernois et al. (1972), and Cherchi and Schroeder (1998). The interval studied shows characteristically 10 to 40 cm-thick, medium light gray and light olive gray (N6, 5Y 6/1) biocalcarenite and biocalcirudite beds with wavy contacts. They include scattered fragments of corals, rudistid and non rudistid bivalves, and brachiopods. They intergrade upward into a 2 m-thick massive bed of sparse calcirudite (floatstone) with rudists (Requeniids). This lithofacies is correlated with Microfacies M10 (Figs. 6–8e–h, 6–9).

6.4.2 CaCO₃ and TOC

Total inorganic carbon (TIC, weight % CaCO₃) and Total organic carbon (TOC, weight % C) measured in Lower Aptian sequence at the Madotz section shows very strong vertical variation with values for TIC ranging from 0 to 98.8%, and TOC from 0 to 1.35% for the whole measured 61 m-thick section.

The lowermost part of the section, between 0 and 3m consists of claystones (Unit 1) contains low CaCO₃ and TOC values; TIC varies from 0 to 6.3%, whereas TOC ranges from 0.2 to 0.5%. A sharp change occurs in the superjacent subunit 2a (3–23 m), which is dominated by biocalcarenites and biomicrudites where TIC suddenly increases and varies between 75.97 and 98.81% (average, 93.93%; n, 15), whereas TOC is nearly 0%. By contrast, the overlying subunit 2b (23 to 47.4 m) shows decreased TIC, while TOC increased relative to infrajacent subunit 2a. From 23 to 42.3 m, TIC and TOC are highly variable (TIC, 8.16–76.76%; TOC, 0.03–1.35%). Bioturbated levels of biocalcirudites, calcilutites and bioclastic marlstones (microfacies M5 and M6) in the lower part of this subunit yielded values for TIC from 35.6 to 76.76%, and TOC between 0 and 1.35%. Soft bioturbated interbeds of claystones, calcareous claystones and marlstones with same faunal assemblages include values for TIC from 14 to 31.53% and TOC

between 0.16 and 0.63%. By contrast, soft interbeds of black marlstone, claystone and clay shale containing rare fossils and dispersive pyrite (microfacies M7, M8) show a drop in TIC with values from 8.16 to 37%, but TOC remain between 0.13 and 1.27%. TIC increases (66.7–97%) in the upper part of subunit 2b (43.3–47.4 m) relative to the lower part of the subunit, and includes a concomitant increase in calcareous biogenic components, whereas TOC values are consistently lower than 0.25%. The trend of increasing TIC (85.55–89.24%) continues into the lower part of subunit 2c (47.4–52.9 m), and TOC lingers lower than 0.17%. Three samples taken between 52.9 m and 61 m, the terminal part of the studied section, yield TIC from 93.35 and 100%, and TOC <0.12%, they coincide with the interval that includes sparse biomicrudites and packed biopelmicrudites with rudistid bivalves indicative of the recurrence of the Urgonian facies.

6.4.3 Microfacies of the Madotz Section: Description and Interpretation

Microscopic analyses of thin sections resulted in the identification of 10 different types of microfacies in the 65.2 m Madotz section. They are summarized in Table 6-1, and illustrated in Figure 6-5 to 6-8. Relative abundance of bioclasts in the thin sections is shown in Figure 6-9.

Microfacies M1. This microfacies occurs at levels ES-06-1 and 3 (Figs. 6-5a and 6-9). It is predominantly terrigenous (TIC, <6.3%), and consists of bioturbated gray-yellowish claystones and silty claystones, with bivalves (tellinoid, nuculoid, arcoid), ammonites and plant remains, as previously described in lithologic Unit 1. Microscopically these claystones are homogeneous and contain less than 1% of silty quartz in a groundmass of clay matrix; fossil fragments are very scattered. The TOC of this Microfacies ranges from 0.2–0.59%.

Interpretation. Claystone is indicative of low energy environment, and the tellinoid, nuculoid, arcoid bivalves, together with the ammonites are fully open marine organisms. The bivalve faunas contain both detritus (tellinoid, nuculoid) and suspension feeders (arcoid) that suggest a quiet well oxygenated depositional environment, with burrowing organisms

(bioturbation index, 3) despite the absence of benthic foraminifers. Abundant plant remains support the closeness of the location to mainland.

Microfacies M2. Microfacies M2 is only found at the base of subunit 2a (3–3.6 m; Fig. 6–5b-c, 6–9), and is dominantly calcareous (TIC, 75.9%; TOC, 0%; level ES-06-4). Microscopically it corresponds to sparse, poorly sorted biomicrite with 30% of bioclasts (wackestone), and up to 7.5% terrigenous quartz. Bioclast sizes range from fine calcarenite to fine calcirudite (~12%), and display high angularity. Orientation of bioclasts' long axes is parallel to stratification or imbricated. The fossil association contains common bivalves (58%), gastropods (4%), echinoids (6%), and agglutinated foraminifers (22%; mostly *Pseudocyclamina hedbergi*, *Choffatella decipiens*, *Marssonella* sp., and textulariids). Pyrite is commonly observed associated with the test of agglutinated foraminifera (~1%) and microbial coatings. Glauconite was scarce (<1%). A low bioturbation index (2) is compatible with good preservation of original orientation of the bioclasts.

Interpretation. The high diversity of marine faunas found in Microfacies M2, the wackestone texture, together with the orientation of bioclasts, provide evidence of a fully marine, oxygenated, moderate to low energy environment with some weak influence of currents. Micritization of fossil walls and microbial coatings indicate a paleobathymetry within the photic zone. Diagenetic pyrite is restricted to potential burial microenvironments generated by microbial activity in the foraminiferal tests. This microfacies is similar in composition to microfacies M9, but microfacies M2 lacks miliolids, and contains abundant gastropods. This facies is indicative of an open marine environment at a depth between the fair weather wave base and the storm wave base.

Figure 6-5 Representative microfossils at the Madotz Section. (A) Microfossils M1, sample ES-06-03; (B, C) microfossils M2, sample ES-06-04; (D, E) microfossils M3, samples ES-06-10 and ES-06-11; (G, H) microfossils M4, samples ES-08-58 and ES-06-14.

Figure 6-6 Representative microfacies at the Madotz Section. (A, B) Microfacies M5, samples ES-06-27, ES-06-38; (C) microfacies M6, sample ES-06-42; (D, E) microfacies M7, samples ES-06-43 and ES-08-20; (F-H) microfacies M8, samples ES-06-44, ES-06-45; ES-06-46. (F) Mechanical accumulation of fossils.

Figure 6-7 SEM images (backscatter mode) on selected samples. (A-D) Microfacies M7, sample ES-06-43, (A) general view of dispersive pyrite, (B-D) details of partially pyritized organic-rich particles by pyrite framboids (B-C,D). (E, H) microfacies M8, sample ES-06-44, (E) dispersed pyrite framboids infilling a *Choffatella* test, (F) pyrite framboids and euhedral crystals infilling a gastropod chamber; (G, H) pyrite framboids and euhedral crystals infilling ostracods and calcispheres.

Figure 6-8 Representative microfacies at the Madotz Section. (A, B) Microfacies M7, sample ES-06-43; (C, D) microfacies M9, sample ES-08-62; (E) microfacies M9/M10, sample ES-08-63; (F-H) microfacies M10, samples ES-08-64, ES-08-65.

Figure 6-9 Relative abundance of the different components of Microfacies M1-M9, based on the counting of bioclasts on 5 random fields in thin sections. Orbitolids (Or), miliolids (M), corals (Co), echinoderms (Ec), rudistid bivalves (R), non-rudistid bivalves (N-R), *Choffatella* and *Pseudocyclammina* (C + P), *Boueina* (B), ostracods (O), calcsphaerae (C).

Microfacies M3. Microscopic assemblages observed between 5.6 and 13 m, and 18 to 23 m (Figures 6–5d–f, 6–9), respectively, characterize Microfacies M3. As described in subunit 2a above, at the field scale these rocks correspond to beds 10–170 cm thick with wavy contacts, and locally channel-like structures.

M3 is a calcareous microfacies (TIC, 85.59–98.81%; TOC, 0%) lacking terrigenous materials, and consists of poorly to moderately sorted biomicrite and fine biomicrudite with 50 to 70% bioclasts. Bioclasts are often rounded and coated with micritic envelopes (cortoids). The fossil assemblage includes fragments of corals (up to 50%), sponges (up to 19%), non-rudistid bivalves (up to 67%), echinoderms (up to 36%), calcareous algae (*Boueina*, up to 31%), bryozoans (up to 9%), and scarce rudists (up to 5%). The texture is grain-supported (packed), and rarely matrix-supported. Matrix consists of micrite, which often shows neomorphic transformation to micro and pseudosparite. A variation of Microfacies M3 is found from 13.2 to 16.5 m (level ES-06-12 and 13, Fig. 6-3), and consists of sparse, poorly sorted biomicrudite with abundant fragments of bivalves (45–61%), echinoderms (24–31%), minor calcareous algae (6–10%), corals (6–7%), sponges and bryozoans (<5%). This minor variant microfacies shows negligible presence of cortoids.

Interpretation. Facies M3 and its variant (packstone and wackestone), comprise abundant rounded fragments that suggest mechanical concentration of bioclastic material in a moderate to high energy environment. This is in agreement with the wavy bedding and occasional channel-shaped strata. Coral fragments are a common component of this microfacies of subunit 2A, but they do not form buildup structures. Also, unlike observations reported elsewhere in Lower Aptian platform and peryplatform series (Bover-Arnal et al., 2009; Masse et al., 2009; Bover-Arnal et al., 2011), the coral fragments do not show microencrusts such as *Lithocodium* -

Bacinella. Abundance of calcareous algae such as *Boueina* sp. (Duvernois et al., 1972) and frequent occurrence of micritic coating of rounded grains indicate that the concentration of bioclastic materials of this microfacies happened in the photic zone (Flügel, 2004).

In the lower Cretaceous, coral-algal assemblages developed in the open outer platform below the wave base, whereas rudist-dominated assemblages occupied more restricted zones in the inner platform (Gili et al., 1995b and references herein). Thus, at Madotz, abundance of coral fragments indicates that these materials were reworked in shoals from assemblages around the platform margin, and they accumulated at a depth between the fair-weather and storm wave base. High diversity of the fossil assemblages together with the absence of terrigenous and organic matter, are indicative of carbonate production under fully oxygenated and oligotrophic conditions away from siliciclastic supplies. The presence of spar is a secondary diagenetic feature related to neomorphism of micrite, which is suggested by incomplete replacement of matrix, and presence of sparite cement in clearly matrix-supported rocks.

The variation of Microfacies M3 described earlier (Fig. 6–9), is here interpreted as representing a low energy, fully marine environment, and the calcareous algae corroborate a depth within the range of the photic zone.

Microfacies M4. It occurs at two levels in subunit 2a: in the lowest part (level ES-06-05 from 5 to 5.6 m; Fig. 6–9), and the middle part (ES-06-14 from 16.5 to 17.4 m; Figs. 6–5h, 6–9), but it is typically developed in the upper part of subunit 2b (from 41.7 to 47.4 m, levels ES-08-54 to 59; Figs. 6–5g, 6–9). Microfacies M4 is predominantly calcareous, poor in organic matter (TIC, 77.6–96.9%; TOC, <0.25%), and includes relatively abundant orbitolinids.

In subunit 2a Microfacies M4 is a sparse biomicrudite and packed peloidal biomicrite characterized by the presence of peloids, cortoids, aggregated grains and conical-shaped orbitolinids. It contains common bivalves (60–62%), benthic foraminifers (*Palorbitolina lenticularis*, textularids; 4–25%), as well as minor echinoids (4%), and corals (1–10%). Other

bioclasts comprise calcareous algae (9%; udoteacean and corallinean), complex lituolid and miliolid foraminifera (2%).

Microfacies association	Description	Main components/features	Subordinate components	Sedimentary and biogenic structures	Texture	Environment
M1	Bioturbated gray claystone and silty claystone	Scarce, highly diverse endobenthic bivalves	Gastropods, ammonites, decapods and wood fragments	Planar bedding. Bioturbation index 3	Matrix-supported, Moderate to high fragmentation	Fine terrigenous off-shore sedimentation. Low energy, fully oxygenated conditions
M2	Sparse, bivalve-lituolid biomicrite	Highly diverse and abundant bioclasts and cortoids. Bivalves, foraminifera (<i>Pseudocyclamina</i> , <i>Choffatella decipiens</i> , <i>Marssonella</i> sp., and textularids)	Echinoderms, gastropods	Imbricated and horizontal bioclasts. Bioturbation index 2	Wackestone texture. Poor sorting. Low fragmentation	Carbonate platform margin/middle ramp. Moderate energy. Mechanical concentration. Fully oxygenated bottom conditions
M3	Sparse and packed coral-bivalve-echinoderm biomicrudites	Highly diverse and abundant bioclasts/cortoids. Corals, calcareous algae (<i>Boueina</i> sp.), non-rudist bivalves, echinoderms	Bryozoans, rudistid-bivalves, sponges	Wavy bedding, rarely channel-like structures. Bioturbation index 1-2	Packstone and wackestone texture. Poor to moderate sorting. High fragmentation and roundness	Photozoan carbonate platform margin/ramp shoal. High-moderate energy. Fully oxygenated bottom conditions
M4	Packed, rounded orbitolinid-echinoderm-bivalve biomicrudites, biomicrites and biopelmicrites	Abundant low diversity foraminifers (<i>Palorbitolina lenticularis</i> both conical and discoidal morphotypes); common cortoids/peloids, non-rudist bivalves and echinoderms	Minor gastropods, brachiopods, <i>Choffatella decipiens</i> , <i>Pseudocyclamina</i> , <i>Lenticulina</i> sp., textularids	Wavy bedding, and wavy lamination. Bioturbation index 1-2	Packstone texture. Poor to moderate sorting. Common fragmented and rounded bioclasts	Heterozoan carbonate platform/ramp shoal. High-moderate energy. Fully oxygenated bottom conditions
M5	Sparse and packed Orbitolinid-bivalve-echinoderm muddy biomicrudites, fossiliferous marlstones, and fossiliferous calcareous claystones	Low diversity assemblage. Common to abundant <i>Palorbitolina lenticularis</i> , echinoderms and non-rudist bivalves.	Serpulids, brachiopods, <i>Choffatella decipiens</i> , <i>Pseudocyclamina</i> sp., <i>Marssonella</i> sp., textularids, <i>Lenticulina</i> sp., calcispheres.	Planar (mudrocks) and wavy bedding (marlstones, limestones). Bioturbation index 1-3. Scoured surfaces in packed biomicrudites	Packstone and wackestone texture. Well and moderate size-sorting (in packed beds), poor size-sorting (in sparse beds) . Low fragmentation and abrasion of bioclasts	Mixed terrigenous-carbonate outer platform/ramp to platform slope. Low to moderate energy. Fully oxygenated bottom conditions

Table 6-1 Summary of the different Microfacies interpreted for the Madotz section.

Table6-1 Continued...

Microfacies association	Description	Main components/features	Subordinate components	Sedimentary and biogenic structures	Texture	Environment
M6	Sparse foraminifer-bivalve-echinoderm muddy biopelmicrites, fossiliferous (silty and sandy) calcareous claystones	Low diversity assemblage. Common <i>Choffatella decipiens</i> , <i>Pseudocyclammia</i> , echinoids and non-rudistid bivalves, pellets	Orbitolinids, textularids	Planar bedding. Bioturbation index 3-4.	Wackestone and mudstone texture. Poor sorting.	Mixed terrigenous-carbonate outer platform/ramp to platform slope. Lower energy than M5. Oxidic bottom conditions
M7	Pyritic, fossiliferous muddy micrites, marlstones, and calcareous claystones, clay-shales, and sandy and silty claystones	Rare bioclasts. Increased framboidal and euhedral pyrite and/of TOC	Rare bivalves, echinoderms, <i>Choffatella decipiens</i> , <i>Pseudocyclammia</i> sp., textularids, <i>Lenticulina</i> sp., calcispheres, ostracods.	Planar bedding. Bioturbation index 2-4 by overprint of bioturbation	Matrix supported fabric (mudstone). Poor sorting	Mixed terrigenous-carbonate outer platform/ramp to platform slope. Low to moderate energy, similar to M6. Short-lived hypoxic conditions
M8	Pyritic calcareous claystones, calcareous clay-shales and clay-shales bearing calcispheres and ostracods	Scarce/rare bioclasts. Common calcispheres and ostracods. Increased framboidal pyrite and organic matter.	Scarce echinoderms, bivalves and <i>Choffatella</i> generally concentrated in laminae	Planar bedding/lamination. Bioturbation index 1-2.	Matrix supported fabric (mudstone). Poor sorting	Mixed terrigenous-carbonate outer platform/ramp to platform slope. Low to moderate energy. Prevalent hypoxic conditions
M9	Sparse and packed miliolid and litiolid biopelmicrites, biomicrudites and biopelmicrudites	Diverse and abundant benthic foraminifers (miliolids, complex litiolids, <i>Choffatella decipiens</i> , textularids). Common pellets, non-rudistid bivalves and echinoids	Minor corals. Rare orbitolinids and small benthic foraminifera	Wavy bedding, large scale cross-stratification. Bioturbation index 1-5	Wackestone and packstone texture. Poor/very poor sorting. Moderate fragmentation, low abrasion.	Photozoan carbonate platform lagoon. Moderate energy. Fully oxidic conditions
M10	Sparse requienid biomicrudites and packed miliolid-rudistid biopelmicrudites	Micritized fragments, diverse and abundant benthic forams (mostly miliolids), requienids, and non-rudistid bivalves. Common micritized bioclastic debris	Minor echinoids, corals, <i>Boueina</i> sp., litiolids, bryozoans, brachiopods	Wavy bedding in packed biopelmicrudites, massive bedding in sparse biomicrudites. Bioturbation index 1-5	Wackestone and packstone texture. Poor to very poor sorting.	Photozoan carbonate inner platform. Moderate energy. Fully oxidic conditions

At the level of subunit 2a this microfacies yields about equal proportion of cortoids and predominantly rounded bioclasts. Conical and discoidal orbitolinid morphotypes are also present in about equal proportion. The matrix as well as bioclasts often displays neomorphism. The bioturbation index shows a value of 3. Glauconite was scarce (<1%).

In the upper part of subunit 2b, Microfacies M4 recurs in association with thicker bedsets (60–180 cm) than in earlier occurrences, and they also show wavy contacts, as well as wavy internal structures. Typically, these beds consist of packed biomicrudite and biopelmicrite. Bioturbation index is commonly low (1–2). The dominant coarse components include 40 to 50% allochems, and the characteristic faunal association consists of abundant *Palorbitolina lenticularis* (16–32%; discoidal and conical morphotypes), non-rudist bivalves (6–14%), echinoderms (10–18%); minor *Pseudocyclamina*, *Choffatella decipiens* (P+C=4–6%), textularids, rare *Lenticulina* sp., brachiopods, gastropods and calcispheres. Bioclasts are commonly rounded and encrusted with micrite (cortoids, peloids) associated with framboidal pyrite (up to 1%). Minor variations occur in the vertical distribution of cortoids that may become locally common. Silt-size quartz is generally less than 2.5%, but can reach as much as 7.5% in some beds.

Interpretation. Microfacies M4 consisting of dominant packed fabric, abundant rounded bioclasts, cyanobacterial coating on rounded bioclasts, as well as ubiquitous presence of wavy stratification suggests a moderately dynamic regime in the photic zone (Flügel, 2004). The coexistence of conical and discoidal orbitolinid morphotypes further supports shallow depths within the platform (Pittet et al., 2002; Bachmann and Hirsch, 2006).

Increasing thickness of beds with packed fabric, including amalgamated thinner wavy beds, moderate-to-poor grain-sorting, points to a wave-dominated depositional environment with varying energy conditions. Low bioturbation index suggests relatively rapid burial events with short time of colonization between events. These beds represent reworked materials accumulated

in shoal environments buried below fair-weather base in the platform margin. Also, low diversity of the fossil assemblage dominated by orbitolinids, and presence of micritic and terrigenous matrix imply increased input of nutrients (Pittet et al., 2002; Bachmann and Hirsch, 2006; Embry et al., 2010).

Microfacies M5. This is a mixed terrigenous-carbonate microfacies occurring at two intervals within unit 2b, between 26.6 and 36 m, and 43.3 to 47.4 m (Figs. 6–6a, 6–9). Its carbonate content varies, and is poor in organic (TIC, 13.4–76.7%; TOC, 0–1.35%). It includes levels of samples ES-08-18a–c, ES-08-19, ES-08-19a–d, ES-08-20b, ES-08-21, ES-06-27, ES-06-38 to 41, ES-06-51 to 53, and ES-08-57, respectively. The main petrographic characteristic of Microfacies M5 is that of a packed and sparse, muddy, fine and medium biomicrudite with common to very abundant specimens of the discoidal morphotype of *Palorbitolina lenticularis*. Allochems vary between 20 and 60%, whereas silt and very fine-size quartz range from 1 to 7.5%. Biogenic components are typically unfragmented and inarticulated. They vary from moderate to well sorted, and are mostly oriented parallel to stratification, or also imbricated. Microfacies M5 also includes bioturbated matrix-supported fossiliferous marlstone, and calcareous claystone (<20% of bioclasts) with the same fossil assemblage, but contain framboidal pyrite in the foraminifera tests (Figure 6–6B), and 1–7.5% of coarse silt to very fine sand-sized quartz included in the matrix.

Predominant fossil components consist of benthic foraminifera (17–43%) with essentially the discoidal morphotype of *Palorbitolina lenticularis* (13–38%). Microfacies M5 also contains fragments of echinoids (0–37%), non-rudist bivalves (1–40%), *Choffatella decipiens*, and *Pseudocyclamina* (C+P=0–21%). Minor fossil constituents include calcispheres (0–40% in claystones), *Lenticulina* sp. (0–7%), textularids, *Marssonella* sp., serpulids and brachiopod fragments. Cortoids and micrite envelopes are absent (except for ES-08-57). Micritization of

shell walls is frequent in benthic foraminifers. Bioturbation index ranges from 1 (in limestones) to 3 (in mudrocks).

Interpretation. Microfacies M5 shows characteristically low diversity fossil assemblages dominated by the discoidal morphotype of *Palorbitolina lenticularis*, *Choffatella decipiens*, echinoids, and non-rudist bivalves. Packed deposits occur in recurring beds that display irregular/wavy lower contact, and imbricated fossils indicative of significant mechanical processes. However, the dominance of whole shells over angular fragments also points to moderate energy conditions. Absence of bioerosion and bioencrustation, and the low bioturbation index (1–2) in densely packed bioclastic beds also indicate relatively rapid burial and short residence time of the bioclasts on the sea bottom. The packed deposits are the result of rapid *in situ* mechanical concentration of allochems from low energy muddy bottoms with similar fossil assemblages. These concentrations may have been the result of stormy conditions.

Orbitolinid-rich facies are reported at different times in Lower Cretaceous series ranging from intertidal and shallow marine carbonate platforms, to low-energy terrigenous well-oxygenated bottoms in the outer platform/ramp and “slope” settings (Vilas et al., 1995; Hughes, 1998; Pittet et al., 2002; Bachmann and Hirsch, 2006; Bover-Arnal et al., 2009; Masse et al., 2009; Embry et al., 2010). Also, based on ranges derived from associated algae, Banner and Simmons (1994) proposed a preferential depth of 10 to 60 m for *Palorbitolina lenticularis*. Orbitolinid episodes have also been related to enhanced supply of nutrients and terrigenous materials due to increased rainfall, weathering and reworking of platform muds during periods of transgression (Pittet et al., 2002 and references herein), as well as with transgressive episodes (e.g. Bachmann and Hirsch, 2006; Bover-Arnal et al., 2009; Embry et al., 2010).

In the Madotz sequence there is no direct association of orbitolinid-rich facies and calcareous algae; but, the morphology of *Palorbitolina lenticularis* in the fossil assemblage corroborates fully oxygenated shallow-water, open marine conditions that received a steady

terrigenous influx of clay and minor silt, most probably between the level between the fair-weather waves and the level of storms. Increase in nutrients as an obvious parameter in covariance with influx of terrigenous materials will be further verified by means of independent geochemical evidence.

Microfacies M6. This Microfacies is also of poorly sorted, mixed terrigenous-carbonate components, low in organic content (TOC, 0–0.79%). It is found in the lower part of subunit 2b, from 28.5 to 36.1 m (levels ES-06-22 to 26, ES-06-29, ES-06-31 to 36, ES-06-42, ES-06-50; Figure 6-5c). It consists of bioturbated muddy, sparse biopelmicrites (Figure 6–5c), made up of 20–30% of allochems including abundant pellets, common non-rudist bivalves (9–44%), echinoderms (13–67%), brachiopods (0–9%), benthic foraminifers (0–27%) and calcispheres (5–18%). Foraminiferal assemblages contain essentially *Pseudocyclamina* and *Choffatella decipiens* (P+C=0–15%), textularids, but rare orbitolinids (0–3%). The bioturbation index is high (3–4). The content of coarse silt and very fine quartz particles varies between 5 and 10%.

Microfacies M6 is also associated with bioturbated fossiliferous silty and sandy calcareous claystones, as well as fossiliferous calcareous claystones which are also low in TOC (0.16–0.8%). Their bioclasts represent less than 5% of the bulk rock and consist of bivalves (0–100%), echinoderms (0–50%), benthic foraminifera (0–39%), calcispheres (0–25%). Orbitolinids are rarely found in these assemblages but *Pseudocyclamina* and *Choffatella decipiens* reach up to 33%. The bioturbation index is high (3). Coarse silt and very fine quartz particles vary between 2.5 and 10%. Disseminated framboidal pyrite occurs as less than 1%, and more rarely as nodules (ES-06-25).

Interpretation. *Choffatella* and *Palorbitolina*, are commonly related to environments with siliciclastic supply (Rey, 1973; Arnaud-Vanneau, 1979), however, *Choffatella* has preference for more quiet environments as observed in shallow platform environments of Portugal (Rey, 1973). The faunal components of Microfacies M6 are indicative, of marine low

energy, quieter, and more distal environments than those represented by *Palorbitolina*-rich Microfacies M5. This interpretation is validated by the matrix-supported fabric of all lithological types corresponding to Microfacies M6. High bioturbation index, very low pyrite and OM content in the fossiliferous silty and sandy calcareous claystones, together with the fossiliferous calcareous claystones indicate relatively long lasting oxygenated conditions in low energy environments between the fair-weather wave base and the storm wave base.

Microfacies M7. This microfacies is characteristically terrigenous and occurs intermittently in the lower part of subunit 2b from 28.5 to 36 m (ES-08-20; ES-06-30, 37; Fig. 6-6d), and between 36 and 38.7m (levels ES-06-43, 47, 49; Fig. 6-7a-d, 6-8a-b).

It includes fossiliferous pyritic marlstones and calcareous claystones, as well as pyritic, bioturbated (bioturbation index, 2–4), fossiliferous calcareous claystones, sandy and silty claystones with moderate to low organic matter (TOC, 0.2–0.9%). Bioclasts are less than 5% including common non-rudistid bivalves (0–50%), echinoids (0–33%), calcispheres (0–67%), ostracods (0–50%), brachiopods (0–7%) and rare benthic foraminifers (0–17%; *Choffatella*, *Pseudocyclammina*, textularids, orbitolonids). Coarse silt and very fine quartz make up 2.5 to 7.5% of the bulk component. Pyrite is present (up to 2.5%) as disseminated framboids and euhedral crystals, infilling of fossil chambers or organic organic debris.

Interpretation. Abundance of fine-grained terrigenous and calcareous matrix characteristic of Microfacies M7 suggests a low energy regime, which is supported by the presence of small and delicate bioclasts such as calcispheres and ostracods. The scarcity of benthic fossils, increased OM, and presence of framboidal pyrite, are compatible with the development of at least occasional suboxic conditions. Nonetheless, evidence of high bioturbation index in some pyritic claystones lacking of benthic foraminifers (ES-06-36, 37), is conceivably a consequence of subsequent biogenic activity during periods of normal oxygenation.

Microfacies M8. This microfacies is equally of fine terrigenous composition, similar to the two preceding microfacies described in the lower part of subunit 2b, but is unique to a 1.8 m-thick bed between 36 and 37.8 m (levels ES-08-44, 45, 46, 48; figs. 6–6f–h; 6–7e–h). It includes calcareous claystones, calcareous clay-shales and clay-shales with very low to absent bioturbation (bioturbation index, 1 or 2), with common well-developed laminae remarkably enriched in pyrite (~1–2.5%) and organic matter (TOC, 0.5–1.27%). Bioclast content is low (<5%), made up of calcispheres (43–62%) and ostracods (17–26%), bivalves (0–4%), echinoderms (0–8%), benthic foraminifers (0–5% *Pseudocyclamina*, *Lenticulina*, *Choffatella*), and ammonites (Gaona-Narvaez et al 2013a). Silt and very fine sand-sized quartz vary from 1 to 5%, but some laminae may contain up to 15%. Benthic foraminifers and most of the macrofossils are generally restricted to the quartz-rich laminae, which can have total fossil content up to 10%. Pyrite is also present as isolated framboids, nodules, or infilling of fossil chambers.

Interpretation. The texture, fabric, and fossil content of Microfacies M8 imply a low energy regime. Development of fine lamination, low bioturbation index, increased framboidal pyrite and total organic matter (TOC), coupled with virtual absence of benthic foraminifers in the quartz-deficient laminae suggest development of suboxic conditions for longer periods than those related to the deposit of microfacies M7. Benthic foraminifers together with other diverse benthic fauna that occur in quartz-rich laminae with irregular lower contact are interpreted as resulting from periodic influx of materials from adjacent proximal oxygenated areas during high-energy events.

Microfacies M9. This calcareous microfacies (TIC, 85.5–89.2%) occurs only between 47.4 and 52.9 m (levels ES-08-59, 60, 61, 61A, 62; Figs. 6–8c–d, 6–9), and is defined in 15–80 cm-thick tabular beds with wavy contacts that locally intergrade with internal large-scale cross bedding. Microfacies M9 comprises sparse, poorly sorted biopelmicrite and biopelmicrudite characterized by a highly diverse fossil assemblage. Texturally this microfacies is equivalent to

wackestone in which allochems fluctuate from 40 to 60% and in most cases show subequal proportions of pellets and bioclasts. Biogenic particles consist of both angular fragments and non-fragmented specimens. Size sorting is poor to very poor, with particles ranging from coarse silt to fine sand size that reach up to 30%. Silt-size quartz is generally less than 2.5%. Pyrite (up to 1%) occurs as partly coating agglutinated foraminifers.

Microfacies M9 comprises fossil assemblages that yield high diversity of benthic foraminifers (30–40.7%) composed of small miliolids (up to 26%), *Choffatella decipiens*, *Pseudocyclamina* (P+C=5–16%), textularids, *Falsogaudryinella*, among others. Other taxa are common non-rudist bivalves (18–34%), echinoderms (6–13%), less frequently orbitolinids (<10%), corals (<1%), brachiopods (<1%), calcispheres (<3%). Cortoids are locally important in some biomicrodites (ES-08-59). Bioturbation index is highly variable (1–5).

Interpretation. The combination of matrix-supported fabric, poor sorting, and dominance of angular fragments points to moderate to low energy conditions pertaining to deposition of Microfacies M9. Wavy primary structures suggest wave influence and local large-scale tabular cross beds indicate subaqueous flow processes related to unidirectional currents. Shallow-water miliolids assemblages are abundant particularly in quiet lagoonal and back barrier areas of recent and ancient carbonate platforms (e.g. Arnaud-Vanneau, 1979; Abed, 1982; Hallock and Glenn, 1986; Hughes, 1998, among others) and are able to tolerate high salinities. *Choffatella* is known to prefer subtidal quiet bottom, and are abundant in lagoons areas with variable salinity (Rey, 1973). Thus, the characteristic benthic foraminiferal assemblages of Microfacies M9 at Madotz provide evidence of a semi-protected shallow subtidal environment (lagoon) at that time, as demonstrated elsewhere in Lower Cretaceous series (Bachmann and Hirsch, 2006). Pittet et al. (2002) also suggested deeper lagoon conditions in oligo-mesotrophic platform environments for a very similar fossil association dominated by wackestones and mudstones.

Microfacies M10. This carbonate Microfacies (TIC, 93.3–100%) has no apparent terrigenous material, and occurs at the base of subunit 2c (levels ES-08-63 to 65, from 52.9 to 62.5 m; Figs. 6-8e-h, 6-9), or the top of the studied section.

Microfacies M10 is associated with an interval composed of 10 to 40 cm-thick beds bounded by wavy contacts. These beds enclose levels of packed biopelmicrudite (packstone, Fig. 6-8f-g), and sparse biomicrudite (wackestone, Fig. 6-8e) made up of 40–60% allochems (peloids, cortoids and bioclasts) showing well-diversified faunal assemblages: rudistid bivalves (3–45%) miliolids (3.2–17%), echinoderm fragments (7–11%), non-rudistid bivalves (5–26%), corals (1–8%), lituolid foraminifers (up to 20% at the base of the designated interval). There are also rare bryozoan, brachiopod, and calcareous algal (*Boueina* sp.) fragments. Bioclasts and cortoids show isotropic fabric, poor size-sorting with subequal proportion of angular and rounded components, ranging from very fine and medium calcirudite to calcarenite, extensively micritized (peloids).. Bioturbation index, 5.

Microfacies M10 also includes zones of sparse biomicrudites showing isotropic fabric, containing about 20% angular bioclasts (wackestone, Figure 6-8h) with low diversity assemblages of large, thick-shelled requieniids (80%), minor fragments of non-rudistid bivalves (8%), rare corals, echinoderms, and lituolid foraminifers. Bioturbation index, 5

Interpretation. The texture (packstone) as well as presence of wavy structures observed in the biopelmicrudites with small requieniids and miliolids are consistent with relatively high energy related to Microfacies M10. Poor sorting of a blend of whole shells, angular and rounded fragments indicates that high energy conditions were not permanent in the environment. Thus, the biopelmicrudites of microfacies M10 developed mostly in shallow subtidal environments of a carbonate platform with varying wave effects. The sparse requeniid-rich biomicrudites represent deeper, quieter conditions of the inner platform (Gili et al., 1995a; Masse et al., 2003) with a depth range of 0.5 to 1 m (Masse et al., 2003).

6.4.4 Pyrolysis

Rock-Eval pyrolysis results from seven samples of the Madotz section are shown in Table 6.2. These results are characterized by low values of free hydrocarbons (S1, 0–0.07 mg HC/g rk), low generatable hydrocarbons (S2, 0–0.4 mg HC/g rk) and low generatable carbon dioxide (S3, 0–0.26 mg CO₂/g rk), as well as low values of hydrogen enrichment index (HI, 1–50 mg HC/g TOC), and oxygen enrichment index (OI, 0–27 mg HC/g rock). All seven samples from the lower part of subunit 2b fall in the field of kerogen type IV when plotted in a pseudo-Van Krevelen diagram (Figure 6-10); such kerogen type corresponds to inert carbon product resulting from either intense alteration and/or oxidation of organic matter in the depositional environment (Tissot and Welte, 1984).

The $T_{\max}$ values obtained vary between 319°C and 446°C, and show an average of 426 °C ($\sigma=47$; n=7), including 6 samples yielding temperatures within the oil window (early to peak oil, Figure 6-11). The transformation ratio ($PI=S1/S1+S2$) shows values from 0–50, and an average PI value of 0.18 (n=7).

Figure 6-10 Classification of kerogen type for selected samples from the Madotz section using a Pseudo-Van Krevelen diagram.

Sample	Total Organic Carbon TOC (%)	Free	Generatable	Total	Hydrogen	Generatable	Oxygen	Transformat ion Ratio "PI" (S1 / S1+S2)	Temp. of Peak S2 Tmax (°C)
		Hydrocarbons S1 (mg HC / gm rk)	Hydrocarbons S2 (mg HC / gm rk)	Hydrocarbon Generation Potential S1+S2 (mg HC / gm rk)	Enrichment Index HI (mg HC / gm TOC)	Carbon Dioxide S3 (mg CO2 / gm rk)	Enrichment Index OI (mg CO2 / gm TOC)		
ES-08-46b	1.27	0.05	0.3	0.35	24	0.21	17	0.14	438
ES-08-18A	1.03	0	0.02	0.02	2	0.26	25	0	445
ES-08-III	0.59	0.01	0.04	0.05	7	0	0	0.2	446
ES-06-23	0.8	0.07	0.4	0.47	50	0.15	19	0.15	445
ES-06-42	0.79	0.01	0.01	0.02	1	0.21	27	0.5	319
ES-06-48	0.58	0.05	0.24	0.29	41	0.13	22	0.17	444
ES-09-52	0.63	0.02	0.15	0.17	24	0.14	22	0.12	446

Table 6-2 Rock-Eval Pyrolysis Results

Figure 6-11 Kerogen typing via plot of hydrogen index vs. T_{max} , and correlation to diagenetic stages of clay minerals (Kübler & Jaboyedoff, 2000). The T_{max} parameter for the Madotz samples fall within the oil window.

6.4.5 Bulk and Clay Mineralogy

Semi-quantitative results on the bulk mineral content of 17 samples from representative lithological types of the Madotz section are shown in Table 6-3. The overall results indicate absence of feldspars and plagioclase, and significant temporal variation in the relative abundance of the mineral content, including clays, quartz, and carbonates (calcite +siderite).The proportions of clays and quartz display strong negative correlation to carbonate (R^2 , 0.85 and 0.9, respectively). The XRD results for the samples analyzed show the following variations: clays, 1–40%; quartz, 3–58%; calcite, 4–95%; siderite, 8–30%; pyrite and marcasite, 0–8%. Figure 6-12 shows the vertical variations of mineral abundance, which highlight the compositional transition between unit 1 and subunit 2a. They clearly bring out a trend of increasing carbonate content

(calcite and siderite from 12% in unit 1, to 93% in subunit 2a), concomitant with decreasing clays (from 40% in unit 1, to 1% in subunit 2a), and quartz (from 46% in unit 1 to 2% in unit 2b). A thin interval associated with an orbitolinid-rich level within subunit 2a (sample ES-06-14, ~17.3m) shows a small increase in the relative abundance of quartz and clays (8% and 17%, respectively) when compared to other samples within subunit 2a.

The compositional difference between subunit 2a and the lower part of superjacent subunit 2b is shown by a sharp increase in clays (6–31%), and quartz (20–44%), while there is a relative decrease in carbonate content (calcite and siderite 73–27%). Worth noting is the interval between 36 and 37.8m of subunit 2b (Figure 6-12) corresponding to unique Microfacies M8 previously discussed that includes the highest proportion of clay (31%) and sulfide (4%), as well as relative low carbonate content (30–33%). Clay contents decrease again (2–11%), in the upper part of subunit 2b whereas quartz is highly variable (3–58%), and carbonate content increases up to 93%. Temporal variation of siliciclastic components continues upward at the base of subunit 2c (Madotz limestone), with clay (2–4%) and quartz (8–11%) remaining constantly low. Sulfides increase in some samples in the lower part of subunit 2c (up to 8%) where they are mostly associated with pyrite formed within the wall of lituolid benthic foraminifera.

Specific clay constituents on 15 samples (Table 6-4, Figure 6-13) yielded moderate and high illite content (46–83%), low to moderate smectite content (0–41%), and rather equally low percentages of kaolinite and chlorite (0–20% each). Illite and smectite are often present as mixed-layer clays; illite is predominant in the claystones and shales of unit 1, as well as in the lower part of subunit 2b, whereas smectite is low or absent (0–1%). Remarkable shifts of clay characteristic occur in the carbonate-rich intervals of subunit 2a, the upper part of subunit 2b, and the lowest part of subunit 2c, respectively. At these levels smectite values may increase from 3 to 41% while illite decreases proportionally. In fact, in general, smectite shows a linear inverse correlation with illite ($R^2=0.8$).

Sample No	Distance from the base in m	Clays	Quartz	K- feldspar	Plagioclase	Calcite	Dolomite	Siderite	Pyrite + Marcasite
ES-08-II	2.8	40%	46%	0%	0%	4%	0%	8%	1%
ES-06-04	3.2	4%	16%	0%	0%	79%	0%	0%	1%
ES-06-05	5	1%	2%	0%	0%	93%	0%	0%	4%
ES-06-14	17.35	8%	17%	0%	0%	75%	0%	0%	0%
ES-08-17	23	1%	3%	0%	0%	95%	0%	0%	0%
ES-06-25	30.65	14%	35%	0%	0%	49%	0%	0%	2%
ES-06-27	31.4	6%	20%	0%	0%	73%	0%	0%	1%
ES-06-37	34.34	26%	44%	0%	0%	19%	0%	8%	3%
ES-08-45A	36.59	31%	36%	0%	0%	18%	0%	12%	4%
ES-08-46B	36.83	27%	33%	0%	0%	23%	0%	13%	4%
ES-08-51	39.31	4%	3%	0%	0%	93%	0%	0%	0%
ES-08-55	44.24	7%	19%	0%	0%	73%	0%	0%	1%
ES-08-57	45.31	11%	58%	0%	0%	30%	0%	0%	0%
ES-08-59	47.66	2%	8%	0%	0%	88%	0%	0%	2%
ES-08-60	49.18	4%	11%	0%	0%	85%	0%	0%	0%
ES-08-61	49.68	2%	8%	0%	0%	53%	0%	30%	8%
ES-08-63	53.09	2%	10%	0%	0%	87%	0%	0%	1%

Table 6-3 Semi-quantitative bulk mineral abundances based on XRD.

Sample No	Distance from the base in m	Smectite	Illite	Kaolinite	Chlorite	Kaolinite/ Chlorite	Kaolinite/ Illite	Kaolinite/ Smectite	Smectite/ Illite
ES-08-II	2.8	0%	80%	8%	12%	0.67	0.10	**	0.00
ES-06-04	3.2	1%	78%	8%	13%	0.62	0.10	8.00	0.01
ES-06-05	5	10%	59%	20%	11%	1.82	0.34	2.00	0.17
ES-06-14	17.35	14%	65%	9%	11%	0.82	0.14	0.64	0.22
ES-08-17	23	28%	61%	3%	8%	0.38	0.05	0.11	0.46
ES-06-25	30.65	1%	83%	9%	7%	1.29	0.11	9.00	0.01
ES-06-27	31.4	1%	83%	7%	9%	0.78	0.08	7.00	0.01
ES-06-37	34.34	0%	79%	10%	10%	1.00	0.13	**	0.00
ES-08-45A	36.59	1%	79%	9%	12%	0.75	0.11	9.00	0.01
ES-08-46B	36.83	1%	78%	9%	12%	0.75	0.12	9.00	0.01
ES-08-51	39.31	34%	46%	0%	20%	0.00	0.00	0.00	0.74
ES-08-55	44.24	3%	83%	11%	4%	2.75	0.13	3.67	0.04
ES-08-57	45.31	41%	47%	12%	0%	**	0.26	0.29	0.87
ES-08-59	47.66	**	**	**	**	**	**	**	**
ES-08-60	49.18	18%	57%	13%	13%	1.00	0.23	0.72	0.32
ES-08-61	49.68	**	**	**	**	**	**	**	**
ES-08-63	53.09	13%	67%	10%	10%	1.00	0.15	0.77	0.19

Table 6-4 Semi-quantitative clay mineral abundances based on XRD. Result not attainable or available **

Figure 6-12 Vertical variation of total organic carbon (TOC) after Gaona Narvaez et al. (2013) and semi-quantitative bulk mineral content (XRD). The black bar indicates the interval corresponding to OAE-1a.

Figure 6-13 Comparison of the stable carbon isotope record ($\delta^{13}\text{C}_{\text{org}}$) after Gaona Narvaez et al. (2013) and semi-quantitative clay mineral content (XRD). The black bar indicates the interval corresponding to OAE-1a; C2-C7 refers to isotopic stages by Menegatti et al. (1998).

6.4.6 Biomarker Analyses

Molecular biomarker indicators were carried out on one sample (ES-08-46B) at the level of Microfacies M8 coincident with the peak of the transgression in the section. The analytical techniques were previously discussed in section 6.3.5; the results include the *n*-alkane, acyclic isoprenoids, saturated biomarkers (steranes, terpanes) and aromatic biomarkers (mono and triaromatic steroids, and triaromatic methylsteroids) are shown in Supplementary Tables 2 to 7. Abundances and ratios are reported based on the area values (Tables 6–5 and 6–6, Supplementary Tables 2 to 7)

The *n*-alkanes range from C11 to C35 (Table 6-5, Figure 6-14), with the highest abundances between C20 to C22. The distribution of *n*-alkanes is slightly shifted toward lower weight homologs, with short chain *n*-alkanes dominated by C17 to C19. No carbon number preference is observed among long-chained *n*-alkanes, so carbon preference indices CPI (Bray and Evans, 1961) and CPI-2 (Marzi et al., 1993), as well as odd-to-even predominance (Scalan and Smith, 1970), OEP, are close to 1.0. Among the isoprenoids Pr/Ph and Pristane/*n*-C17 have values of 0.88 and 0.28, respectively.

Regular steranes (C27–C30) (Table 6-6, Supplementary Table 4), dominate their distribution (*m/z* 217 ion chromatograms), whereas rearranged molecules or diasterane abundances are low. Among the regular steranes C29 is just slightly more abundant than C27 and C28. Isomerization at C-20 in the C29 5 α , 14 α 17 α (H)-steranes given as the 20S/(20S + 20R) ratio has a value of 0.3. Isomerization at C-14 and C-17 in the C29 20S and 20R regular steranes expressed as the $\beta\beta$ S/($\beta\beta$ S+ $\alpha\alpha$ R) ratio shows a value of 0.56.

Hopanoids (*m/z* 191 ion chromatograms) (Table 6-6, Supplementary Table 4) are relatively abundant in regard to steranes. The C31-35 17 α 22S and 22R homohopane distribution shows C31>32>C33> C34>C35. The Madotz sample gave a value of 0.04 for the C35 homohopane Index (C35/C31–35). The C31 and C32 17 α -homohopanes isomerization at C22

given by $22S/(22S + 22R)$ ratios yielded values of 0.59. The ratio of 17β , $21\alpha(H)$ -moretanes to 17α , $21\beta(H)$ -hopanes, measured using abundance of the C30 homolog, produced a value of 0.17. Gammacerane (pentacyclic terpenoid) is reported in the sample (6991 area).

Aromatic hydrocarbons (aryl hydrocarbons) are characterized by absence of C27 to C29 monoaromatic steroid (MA) (Supplementary Table 6). Among the triaromatic steroids (TAS), TAS29 is absent. The steroid aromatization ratio $TA28/(TA28+MA29)$ has a value of 1 (100%). Triaromatic dinosteroids (biomarkers for dinoflagellates) are relatively abundant.

Figure 6-14 Gas chromatogram of the saturated hydrocarbon extract of sample ES-08-46B. Regular isoprenoids (IP), and normal alkanes (NC) are labeled according to their carbon number. Pristane= IP19, Phytane=IP20.

Peak Label	Compound Name	ES-06-46B		
		Ret. Time	Area	Height
NC9	Normal Alkane C9			
NC10	Normal Alkane C10			
IP11	Isoprenoid C11			
NC11	Normal Alkane C11	8.585	78	35
NC12	Normal Alkane C12	11.264	150	63
IP13	Isoprenoid C13	11.651	36	12
IP14	Isoprenoid C14	13.275	41	16
NC13	Normal Alkane C13	14.025	244	100
IP15	Isoprenoid C15	16.129	84	32
NC14	Normal Alkane C14	16.748	406	156
IP16	Isoprenoid C16	18.402	172	49
NC15	Normal Alkane C15	19.376	935	340
NC16	Normal Alkane C16	21.89	5731	2248
IP18	Isoprenoid C18	23.077	2090	481
NC17	Normal Alkane C17	24.292	24541	8936
IP19	Isoprenoid C19 (Pristane)	24.434	6839	1665
NC18	Normal Alkane C18	26.557	44340	16444
IP20	Isoprenoid C20 (Phytane)	26.768	7763	1747
NC19	Normal Alkane C19	28.631	58783	22357
NC20	Normal Alkane C20	30.544	65538	24643
NC21	Normal Alkane C21	32.325	65620	25009
NC22	Normal Alkane C22	33.996	61640	23734
NC23	Normal Alkane C23	35.575	56051	21578
NC24	Normal Alkane C24	37.075	52613	18919
NC25	Normal Alkane C25	38.506	47198	17112
NC26	Normal Alkane C26	39.876	38645	14343
NC27	Normal Alkane C27	41.192	31526	11937
NC28	Normal Alkane C28	42.458	25224	9478
NC29	Normal Alkane C29	43.68	20266	7717
NC30	Normal Alkane C30	44.86	15316	5272
NC31	Normal Alkane C31	46.004	11456	3563
NC32	Normal Alkane C32	47.185	7308	1810
NC33	Normal Alkane C33	48.487	5752	820
NC34	Normal Alkane C34	49.952	3312	281
NC35	Normal Alkane C35	51.787	1084	88
NC36	Normal Alkane C36			
NC37	Normal Alkane C37			
NC38	Normal Alkane C38			
NC39	Normal Alkane C39			
NC40	Normal Alkane C40			
Ratios				
Pristane/Phytane			0.880974	
Pristane/nC17			0.278677	
Phytane/nC18			0.175079	
nC18/nC19			0.7543	
nC17/nC29			1.210944	
CPI Marzi			1.003438	
CPI Bray & Evans			1.064	
OEP (1) Scalan & Smith			0.98	
OEP (2) Scalan & Smith			1	
Resolved Components (%)				
Normal Paraffins			62.52065	
Isoprenoids			1.653441	
Resolved unknowns			35.82601	

Table 6-5 Results of the GC analysis of the saturated hydrocarbon fraction extracted from the shale sample ES-08-46B, corresponding to microfacies M8. Carbon preference index CPI-1 (Bray and Evans, 1961) and CPI-2 (Marzi et al., 1993), as well as odd-to-even predominance (OPI, Scalan and Smith, 1970).

RATIOS (on Areas)	ES-08-46B
Steranes (<i>m/z</i> 217; 218)	
%C ₂₇ ∇BBS (218)	31.36
%C ₂₈ ∇BBS S (218)	28.47
%C ₂₉ ∇BBS S (218)	40.17
%C ₂₇ ∇∇∇R (217)	34.64
%C ₂₈ ∇∇∇R (217)	28.00
%C ₂₉ ∇∇∇R (217)	37.36
S/(S+R) (C ₂₉ ∇∇∇) (217)	0.30
BBS/(BBS+∇∇R) (C29) (217)	0.46
(C ₂₁ +C ₂₂)/(C ₂₇ +C ₂₈ +C ₂₉) (217)	0.20
C ₂₇ /C ₂₉ (∇BBS S) (218)	0.78
C ₂₈ /C ₂₉ (∇BBS S) (218)	0.71
Diaster/∇∇∇ Ster (C ₂₇) (217)	0.77
C30 ∇BBS Sterane Index (218)	3.97
C30 S+R Sterane Index (218)	4.54
Terpanes (<i>m/z</i> 191)	
Oleanane/Hopane	
Gammacerane/Hopane	0.22
Norhopane/Hopane	0.72
Bisnorhopane/Hopane	
Diahopane/Hopane	0.29
Moretane/Hopane	0.17
25- <i>nor</i> -hopane/hopane	
Ts/(Ts+Tm) trisnorhopanes	0.32
C29Ts/C29 Hopane	0.22
H32 S/(R+S) Homohopanes	0.59
H35/H34 Homohopanes	0.61
C24 Tetracyclic/Hopane	0.39
C24 Tetracyclic/C26 Tricyclics	7.47
C23/C24 Tricyclic terpanes	2.33
C19/C23 Tricyclic terpanes	1.14
C26/C25 Tricyclic terpanes	0.80
(C28+C29 Tricyclics)/Ts	0.36
Various (<i>m/z</i> 191; 217)	
Steranes/Hopanes	0.14
Tricyclic terpanes/Hopanes	0.38
Tricyclic terpanes/Steranes	2.78

Table 6-6 Results of the GC-MS analysis of the saturated hydrocarbon fraction extracted from the shale sample ES-08-46B, corresponding to microfacies M8.

6.4.7 Elemental Analyses

6.4.7.1 *Major and Minor elements*

Major and minor elemental concentrations were obtained from a range of lithologies (clay-shales to muddy limestones) on 19 samples of subunit 2b (Table 6-7, Figure 6-18). Claystones/shales yielded the following average concentrations: Si=21.25%, Al=13.23%, K=3.33%, Fe=3.76%, Ca=5.18%, Mg=0.94%, Ti=0.85%, P=523 ppm and Mn=169.6 ppm. Calcareous shales show average concentrations as follows: Si=9.3%, Al=10.17%, K=3.09%, Fe=3.16%, Ca=8.83%; Mg=0.8%, Ti=0.49%, P=867.73 ppm and Mn=185.1 ppm. The more carbonate-rich levels such as marlstones and limestones yielded averages of: Si=18.07%, Al=4.93%, K=1.73%, Fe=1.7%, Ca=17.58%, Mg=0.49%, Ti=0.77%, P=431.69 ppm, and Mn=206.8 ppm.

Si, K, Fe, Mg and Ti contents show strong positive correlation with Al ($R^2=0.88, 0.84, 0.86, 0.82$, and 0.62 , respectively); Figure 6-15a, b, d, e. On the other hand, Fe also shows good positive correlation with TIC ($R^2=0.66$). The peak values for Al, Si, K, Fe, Mg and Ti occur within the interval from 36 to 37.8 m that coincides with the thickest level of claystones and shales within subunit 2b (Table 6-7, Figure 6-18), concurrent with the most important peak of TOC in the section. Nevertheless Al, Si, K, Fe and Mg correlate poorly with TOC and such correlation is possitive ($R^2=0.27, 0.12, 0.1, 0.26$, and 0.2 , respectively).

Phosphorous values range from 343 to 2893 ppm, and show three apparent peaks (Figure 6-18) within calcareous claystone beds at 27.56 (1655 ppm), 33.9 (1156 ppm), and 34.86 m (2893 ppm). Total phosphorous is moderately correlated with Al ($R^2=0.45$, Figure 6-15e) whereas total P shows negative correlation with TOC ($R^2=0.13$), and P/Al is uncorrelated with TOC ($R^2=0.05$).

Figure 6-15 Variation of different major and minor elements with respect to Aluminum for 19 selected samples of the Madotz section.

Figure 6-16 Variation of different trace elements with respect to Aluminum for 19 selected samples of the Madotz section.

Figure 6-17 Variation of different minor and trace elements with respect to calcium and total organic carbon (TOC) for 19 selected samples of the Madotz section.

Figure 6-18 Variation in the total concentration of major and minor elements and TOC in subunit 2b of the Madotz section correlative with stable carbon isotope stages C4 and C5 (TOC after Gaona-Narvaez et al., 2013)

Manganese shows weak, negative correlation with both Al and TOC ($R^2=0.13$ and 0.2 , respectively), Figure 6-16f. Also, Mn/Al exhibits good positive correlation with Ca ($R^2=0.79$, Figure 6-17b) and weak negative correlation with TOC ($R^2=0.19$, Figure 6-17c). Peak values for Mn and Mn/Al occur in a pelletal limestone at 30.1 m.

6.4.7.2 Trace elements

Trace element values in the samples from subunit 2b show an overall small temporal variation (Table 6-7) as the pattern in the concentrations of V, Cr, and Ni is very consistent with that of Al. Bivariate plots (Figure 6-16a-c) corroborate the strong positive correlation between these elements and Al ($R^2= V 0.92$, Cr 0.94 , Ni 0.94 , respectively). The total concentrations for these elements show a weak positive correlation with TOC ($R^2=0.12$, 0.17 , 0.2). Nonetheless,

correlation of V/Al, Cr/Al with TOC is negative ($R^2=0.09$, 0.3), and Ni/Al is uncorrelated to TOC. Total concentrations of Zn, As, Ba, and Th show positive correlation with Al ($R^2=0.53$, 0.58 , 0.74 and 0.6 , respectively; Figure 6-15h, Figure 6-16e-h), but U ($R^2=0.23$; Figure 6-16h) and P ($R^2=0.045$; Figure 6-15e) show poor positive correlation with Al. Cobalt seems uncorrelated with Al (Figure 6-16d).

Element ratios such as Co/Al ($R^2=0.07$), As/Al ($R^2=0.1$), Ba/Al ($R^2=0.27$), and U/Al ($R^2=0.35$) show negative correlation with TOC, although Zn/Al ($R^2=0.0016$) shows no correlation with TOC. Ba/Al shows a very weak positive correlation with Ca ($R^2=0.16$).

Figure 6-19 Variation of selected minor and trace elements normalized to Al in subunit 2b of the Madotz section correlative with stable carbon isotope stages C4 and C5. TOC data after Gaona-Narvaez et al. (2013). All Element/Al ratio $\times 10^{-4}$

Table 6-7 Major, minor and trace element concentrations from the Madotz Section, obtained by LA-ICP-MS

Sample No	ES 08 19a	ES 06 22	ES 06 23	ES 06 24	ES 06 26	ES 06 25	ES 06 28	ES 06 30	ES 06 34	ES 06 36	ES 06 37
TOC	0.31	0.26	0.80	0.24	0.38	0.39	0.41	0.48	0.16	0.31	0.39
TIC	16.89	27.12	20.02	66.19	33.73	36.99	21.73	14.09	25.41	21.12	16.52
Al (wt%)	13.03	8.96	9.48	3.20	5.93	5.67	9.70	15.32	6.86	8.00	11.30
Si (wt%)	24.25	15.38	17.30	5.84	10.36	11.71	17.89	26.59	15.90	14.61	20.70
Ca (wt%)	8.10	11.46	9.21	21.94	13.19	17.62	10.40	6.25	12.06	11.19	8.03
Fe (wt%)	3.36	2.62	2.66	1.28	2.07	1.74	2.69	1.64	2.15	2.86	3.82
K (wt%)	4.44	2.49	2.93	0.91	1.66	1.81	3.13	4.80	2.20	2.22	3.70
Mg (wt%)	0.90	0.71	0.72	0.48	0.49	0.51	0.76	1.26	0.59	0.76	0.87
Ti (wt%)	0.85	0.71	0.74	0.36	0.59	0.55	0.75	1.10	0.79	0.77	0.85
Ti/Al	0.07	0.08	0.08	0.11	0.10	0.10	0.08	0.07	0.11	0.10	0.07
EF Ti	1.30	1.59	1.56	2.25	1.98	1.92	1.55	1.44	2.29	1.94	1.50
P (ppm)	1655	605	656	397	398	500	591	1462	643	1156	757
P/Al*	127.1	67.5	69.2	124.1	67.2	88.2	60.9	95.4	93.6	144.5	67.0
EF P	1.3	0.7	0.7	1.2	0.7	0.9	0.6	1.0	0.9	1.4	0.7
Mn (ppm)	191	203	156	234	186	200	174	178	184	222	189
Mn/Al*	14.6	22.7	16.4	73.3	31.4	35.2	17.9	11.6	26.7	27.8	16.7
EF Mn	0.2	0.2	0.2	0.8	0.3	0.4	0.2	0.1	0.3	0.3	0.2
V (ppm)	112	77	76	27	47	43	95	156	62	80	103
V/Al*	8.6	8.6	8.1	8.4	7.9	7.6	9.8	10.2	9.0	10.0	9.2
EF V	0.6	0.6	0.5	0.6	0.5	0.5	0.7	0.7	0.6	0.7	0.6
Cr (ppm)	111	82	80	31	58	48	84	140	66	80	100
Cr/Al*	8.5	9.1	8.5	9.7	9.9	8.5	8.7	9.1	9.5	10.0	8.8
EF Cr	0.8	0.9	0.8	1.0	1.0	0.8	0.8	0.9	0.9	1.0	0.9
Co (ppm)	13	12	9	9	9	17	23	15	16	21	22
Co/Al*	1.0	1.3	1.0	2.9	1.5	2.9	2.3	1.0	2.3	2.7	1.9
EF Co	0.5	0.6	0.5	1.4	0.7	1.4	1.1	0.5	1.1	1.3	0.9

Table 6-7 Continued...

Sample No	ES 06 38	ES 06 43	ES 06 44	ES 06 45	ES 08 46b	ES 06 46	ES 06 47	ES 06 49	Average shale	Coefficient of variation	Average of σ
TOC	0.19	0.70	0.56	0.90	1.28	0.97	0.91	0.41			
TIC	24.35	18.94	17.03	13.36	16.47	8.16	9.12	17.28			
Al (wt%)	9.03	7.33	11.33	13.31	11.36	14.34	12.13	10.77	8.84	0.03	0.26
Si (wt%)	18.20	12.43	17.46	20.37	20.43	22.21	20.31	19.44	27.53	0.06	0.98
Ca (wt%)	11.52	6.12	7.58	6.70	8.37	4.64	5.73	6.70	1.57	0.02	0.21
Fe (wt%)	3.18	2.40	3.89	4.10	4.16	3.91	3.61	3.23	4.80	0.02	0.08
K (wt%)	3.04	1.58	3.10	3.88	3.71	3.82	2.85	3.33	2.99	0.06	0.20
Mg (wt%)	0.86	0.65	0.83	0.91	1.08	0.99	0.91	0.81	1.60	0.03	0.02
Ti (wt%)	0.84	0.54	0.79	0.86	0.71	0.86	0.86	0.81	0.46	0.10	0.04
Ti/Al	0.09	0.07	0.07	0.06	0.06	0.06	0.07	0.08	0.05		
EF Ti	1.85	1.48	1.39	1.29	1.25	1.19	1.41	1.51			
P (ppm)	2893	364	539	519	617	522	524	547	700	0	45
P/Al*	320.5	49.7	47.6	39.0	54.3	36.4	43.2	50.8	100.0		
EF P	3.2	0.5	0.5	0.4	0.5	0.4	0.4	0.5			
Mn(ppm)	210	152	190	193	208	159	181	170	850	0.03	5.43
Mn/Al*	23.3	20.8	16.7	14.5	18.3	11.1	14.9	15.7	96.0		
EF Mn	0.2	0.2	0.2	0.2	0.2	0.1	0.2	0.2			
V (ppm)	82	64	102	103	97	121	102	94	130	0.02	1.95
V/Al*	9.1	8.7	9.0	7.8	8.5	8.4	8.4	8.7	14.7		
EF V	0.6	0.6	0.6	0.5	0.6	0.6	0.6	0.6			
Cr (ppm)	79	61	101	103	101	115	100	92	90	0.04	2.85
Cr/Al*	8.7	8.3	8.9	7.7	8.8	8.0	8.2	8.6	10.2		
EF Cr	0.9	0.8	0.9	0.8	0.9	0.8	0.8	0.8			
Co (ppm)	11	11	10	12	14	17	34	17	19	0.10	1.60
Co/Al*	1.2	1.5	0.9	0.9	1.2	1.2	2.8	1.6	2.1		
EF Co	0.6	0.7	0.4	0.4	0.6	0.6	1.3	0.7			

Table 6-7 Continued...

Sample No	ES 08 19a	ES 06 22	ES 06 23	ES 06 24	ES 06 26	ES 06 25	ES 06 28	ES 06 30	ES 06 34	ES 06 36	ES 06 37
Ni (ppm)	42	26	27	10	19	16	30	57	22	25	37
Ni/Al*	3.2	2.9	2.8	3.2	3.2	2.8	3.1	3.7	3.2	3.1	3.3
EF Ni	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.5	0.4	0.4	0.4
Zn (ppm)	94	78	98	66	55	44	80	91	50	70	99
Zn/Al*	7.2	8.7	10.3	20.7	9.2	7.7	8.3	5.9	7.3	8.7	8.7
EF Zn	0.7	0.8	1.0	1.9	0.9	0.7	0.8	0.6	0.7	0.8	0.8
As (ppm)	19	10	12	4	6	5	14	19	10	14	23
As/Al*	1.4	1.1	1.2	1.2	1.0	1.0	1.4	1.3	1.5	1.8	2.1
EF As	1.3	1.0	1.1	1.1	0.9	0.9	1.3	1.1	1.4	1.6	1.9
Ba (ppm)	620	520	496	163	421	294	475	705	457	481	699
Ba/Al*	47.6	58.0	52.3	51.0	71.1	51.9	49.0	46.0	66.6	60.1	61.9
EF Ba	0.7	0.9	0.8	0.8	1.1	0.8	0.7	0.7	1.0	0.9	0.9
Th (ppm)	13	13	12	6	9	9	11	15	10	11	13
U (ppm)	2	3	2	1	2	2	2	3	2	2	3
U/Al*	0.2	0.4	0.2	0.3	0.3	0.3	0.2	0.2	0.3	0.3	0.2
EF U	0.4	0.9	0.6	0.9	0.7	0.7	0.5	0.5	0.8	0.7	0.6
V/Cr	1.0	0.9	1.0	0.9	0.8	0.9	1.1	1.1	0.9	1.0	1.0
V/(V+Ni)	0.7	0.7	0.7	0.7	0.7	0.7	0.8	0.8	0.7	0.8	0.7
Ni/Co	3.2	2.3	2.8	1.1	2.2	0.9	1.3	3.9	1.3	1.2	1.7
U/Th	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2

Enrichment factors (EF) calculations are based on average shale values by Wedepohl(1971, 1991)

*=(*10⁻⁴)

Values in bold and italic: average values of 4 replicates with coefficient of variation higher than 0.15

Table 6-7 Continued...

Sample No	ES 06 38	ES 06 43	ES 06 44	ES 06 45	ES 08 46b	ES 06 46	ES 06 47	ES 06 49	Average shale	Coefficient of variation	Average of σ
Ni (ppm)	29	23	34	41	37	44	38	32	68	0.04	1.05
Ni/Al*	3.2	3.2	3.0	3.1	3.2	3.1	3.2	3.0	7.7		
EF Ni	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4			
Zn (ppm)	69	77	109	119	98	134	144	84	95	0.08	7.33
Zn/Al*	7.6	10.5	9.7	9.0	8.6	9.3	11.9	7.8	10.7		
EF Zn	0.7	1.0	0.9	0.8	0.8	0.9	1.1	0.7			
As (ppm)	13	11	13	13	11	16	17	15	10	0.10	3.37
As/Al*	1.4	1.5	1.1	0.9	1.0	1.1	1.4	1.4	1.1		
EF As	1.3	1.4	1.0	0.9	0.9	1.0	1.3	1.3			
Ba (ppm)	431	285	574	584	512	618	547	509	580	0.06	33.21
Ba/Al*	47.8	38.9	50.7	43.9	45.0	43.1	45.1	47.3	65.6		
EF Ba	0.7	0.6	0.8	0.7	0.7	0.7	0.7	0.7			
Th (ppm)	11	9	14	14	11	15	14	12		0.12	1.37
U (ppm)	3	1	2	2	2	2	3	3	4	0.17	0.39
U/Al*	0.3	0.2	0.2	0.2	0.2	0.2	0.3	0.2	0.4		
EF U	0.8	0.4	0.4	0.4	0.5	0.4	0.7	0.6			
V/Cr	1.0	1.0	1.0	1.0	1.0	1.1	1.0	1.0			
V/(V+Ni)	0.7	0.7	0.8	0.7	0.7	0.7	0.7	0.7			
Ni/Co	2.6	2.2	3.4	3.4	2.6	2.5	1.1	1.9			
U/Th	0.3	0.1	0.1	0.2	0.2	0.2	0.2	0.2			

Enrichment factors (EF) calculations are based on average shale values by Wedepohl(1971, 1991)

*=($\times 10^{-4}$)

Values in bold and italic: average values of 4 replicates with coefficient of variation higher than 0.15

Interelemental ratios for V/Cr, Ni/Co, V/(V+Ni) and U/Th are uncorrelated with TOC values, and show little variation V/Cr (0.8–1.12), V/(V+Ni) (0.71–0.75), U/Th (0.15–0.26), and Ni/Co (1.15–3.44) (Table 6-7). The following small shifts are observed from the overall temporal variation of elemental components normalized to Al (

Figure 6-19):

- (a) Small increase in the Co/Al, U/Al, Zn/Al ratios at 30.1 m (pelletal limestone, ES-06-24), also coincident with Mn/Al maximum.
- (b) Minima for U/Al, and Co/Al occur at 32.76 m (ES-06-30), corresponding to relatively high Ba/Al and relatively low Mn/Al and As/Al.
- (c) Two levels of relatively high values of Co/Al, U/Al, Ba/Al, Mn/Al, at 33.42 m and 33.9 m (ES-06-34, 36, respectively).
- (e) An interval between 36 and 37.7 m (ES-06-43 to 49) of low Mn/Al and Ba/Al ratios, showing a drop followed by a slight increase in the values of Co/Al, As/Al and Zn/Al.

6.5 Discussion

6.5.1 Thermal Maturation of the Organic Matter

Thermal maturation of the organic matter is interpreted from the kerogen using Rock-Eval pyrolysis (Table 6–2, Figure 6-11) and from the bitumen using aliphatic and aromatic biomarker transformations (Figure 6-14, Tables 6–3, Supplementary Tables 2 to 7).

The stage of thermal maturation of a source rock can be related to the Rock-Eval pyrolysis parameter $T_{\max}$, which is the temperature of maximum hydrocarbon release during thermal decomposition (S2 peak). Maturation processes also cause reduction in the TOC and HI values as hydrocarbon is generated and expelled (Dembicki, 2009). The $T_{\max}$ values obtained vary between 319°C and 446°C, including 6 samples yielding temperatures within the oil window (early to peak oil, Figure 6-11). These results show general agreement with the results of the following biomarker parameters obtained from a single sample extract (sample ES-08-46B):

- 1) The distribution of *n*-alkanes is displaced toward lower weight homologs. Also, carbon preference indices (CPI, Bray & Evans, 1961; CPI-2, Marzi et al., 1993) and odd-to-even predominance (OEP, Scalan & Smith, 1970) are close to 1.0. No apparent C-number preference in mature samples is a result of the dilution effect caused by the random cleavage of alkyl chains in the kerogen matrix source of *n*-alkanes, and/or the loss of high-OEP components during hydrocarbon expulsion (Killops and Killops, 2005).
- 2) Isomerization at C-20 in the C29 5 α , 14 α 17 α (H)-steranes (*m/z* 217 mass chromatograms) is expressed as the 20S/(20S + 20R) ratio. This parameter is based on the relative enrichment of the 20S isomer relative to the biologically derived 20R isomer, and reaches a value of 0.3 in the sample analyzed. Use of S/(S+R) C29 $\alpha\alpha\alpha$ steranes requires calibration for each basin. However Peters et al. (2005b) argued study cases in which the generation starts at isomerization ratios as low as 0.23, and as high as 0.4; equilibrium is reached between 0.5 and 0.55 within the peak oil stage.
- 3) Isomerization at C-14 and C-17 in the C29 20S and 20R regular steranes (*m/z* 217 mass chromatograms), expressed as $\beta\beta S/(\beta\beta S + \alpha\alpha R)$ ratio (or $\beta\beta S\%$), show a value of 0.56 (56%) in the Madotz sample. This C29-sterane isomerization ratio reaches values of 0.25 ($\sim Ro\%$, 0.6) within the early oil window, and then, attains equilibrium at values between 0.67 and 0.7 ($\sim Ro\%$, 0.9), at the beginning of the late oil generation (Peters et al., 2005b).
- 4) C31 and C32 17 α -homohopanes isomerization at C22 (*m/z* 191 mass chromatograms) expressed as 22S/(22S + 22R) ratio documents the relative enrichment of the more thermally stable 22S isomer compared to the biologically occurring 22R isomer. 22S/(22S + 22R) ratios yield values of 0.59 for the Madoz sample, which would imply that the main phase of oil generation has been reached or surpassed, because 17 α -homohopane isomerization reaches equilibrium between 0.57 and 0.62 during early oil generation (Seifert and Moldowan, 1980).

- 5) Maturation of monoaromatic steroid (MA) yields triaromatic steroids with one less carbon. The monoaromatic steroid aromatization ratio $TA_{28}/(TA_{28}+MA_{29})$ increases from 0 to 100% during thermal maturation, and it has a value of 1 (100%) in the studied sample. This value suggests that the sample maturity has been reached, and the sample is or surpassed the peak oil stage (Peters et al., 2005b).
- 6) The ratio of 17β , $21\alpha(H)$ -moretanes to 17α , $21\beta(H)$ -hopanes, measured using abundance of the C30 homolog, shows a value of 0.17 for the Madotz sample, which would indicate conditions close to thermal maturity. Moretane/Hopane ratios diminish with thermal maturity from ~0.8 in immature bitumens to <0.15 in mature sources and oils; equilibrium conditions are reached at values of 0.05 (Peters et al., 2005). Moretane/hopane ratios are known to be sensitive to source input and paleoenvironment, and increase with inputs from terrestrial higher plants inputs (Isaksen and Bohacs, 1994). Terrestrial inputs are confirmed for the studied sample in which *n*-alkanes C27, C29 and C31 are present, and potentially affected the original moretane/hopane ratio of the sample, influencing the maturity interpretation.

These parameters taken as a group would suggest conditions within the oil window, ranging from early oil to peak oil generation stages.

6.5.2 Sources of the Organic Matter

Assessment of the relative contributions of autochthonous marine versus terrigenous organic matter in the Madotz sample (from a bed sitting on top of the maximal flooding surface of the section) is complicated by the maturity level of the sample. Supply of allochthonous OM from the continent is demonstrated by the presence of long chain *n*-alkanes >C22 with odd-numbers (particularly C27, C29, C31, Table 6-5, Figure 6-14) originated from higher plant epicuticular waxes (Eglinton and Hamilton, 1967; Peters et al., 2005b). Allochthonous OM in provenance of higher plants seems important according to the record of C27 to C29 $\alpha\alpha\alpha$ -20R

steranes in which the abundance of the C29 sterane is slightly higher than in plankton and algae-derived C27 and C28 steranes (Huang and Meinschein, 1979). Steranes/Hopanes ratios reflect eukaryote versus prokaryote inputs; its low value at Madotz (0.14) points toward significant supply of terrigenous material and/or microbially altered organic matter (Tissot & Welte, 1984, Peters et al., 2005b). This interpretation is in agreement with the results of Rock-Eval pyrolysis, which indicate a kerogen type IV (very low H/C ratio and a variable O/C atomic ratio; low Rock-Eval HI, <50 mg HC/g TOC), characteristic of inert carbon with no oil generation potential (mostly inertite and minor vitrinite). These results indicate either intense alteration and/or oxidation of organic matter on land and subsequent transport to the depositional site, or organic matter severely altered/oxidized in the depositional environment (Tissot & Welte, 1984; Killops & Killops, 2005; Peters et al., 2005b); see further discussion in the section on redox conditions.

In counter argument, the low pristane/phytane and pristane/*n*-C17 ratios (0.88 and 0.28, respectively) would be compatible with dominance of marine-derived materials (Peters et al., 2005). Since these ratios are based on compounds derived from organisms bearing chlorophyll, and oxidation is typical of the terrigenous OM, the actual values obtained suggest that the OM in the studied sample underwent limited oxidation. Maturation of the OM however has the tendency to increase the Pr/Ph ratio while decreasing the Pr/*n*-C17 ratios.

Marine phytoplankton sources are also indicated by contributions of odd-numbered *n*-alkanes < C22 (Table 6-5, Figure 6-14) mostly contributed by algae (*n*-C15, *n*-C17, *n*-C19); and cyanobacteria (*n*-C17), (Gelpi et al., 1970; Blumer et al., 1971; Peters et al., 2005b, 2005a). Furthermore, dinoflagellates contribution can be recognized in the sample by the presence of triaromatic dinosteroids (Supplementary Tables 6, 7), originated from dinosterols, which are structurally related to 4, 23, 24-trimethylcholesterols and are very abundant in modern dinoflagellates (Peters et al., 2005b; Li et al., 2012).

6.5.3 Evidence for Redox Conditions from Pyrolysis and Biomarkers

Seven samples selected from Unit 1 and 2b, fall in the field of kerogen type IV when plotted in a pseudo-Van Krevelen diagram (Figure 6-10, Table 6-2). This kerogen type is characterized by very low H/C ratio and a variable O/C atomic ratio, which is typical of inert organic carbon with no oil generation potential, due to intense alteration and/or oxidation of land-derived organic matter, or organic matter severely altered/oxidized in the depositional environment (Tissot & Welte, 1984; Killops & Killops, 2005; Peters et al., 2005b).

This characterization of the kerogen from the sample analyzed is in agreement with the microfacies evidence for most, but two samples (ES-08-46B, ES-06-48; see Microfacies M8). Biomarkers in ES-08-46B provided evidence (high Gammacerane, and pristane/phytane <1) consistent with the development of stratification and reducing conditions.

Nonetheless, judicious use of these parameters is necessary, because discrimination of kerogen based on bulk rock HI and OH can be affected by the degree of thermal maturation of the samples, degree of bioturbation of the sediment, degree of mixture between two or more kerogen types, and artifacts created during pyrolysis of the sample. Such artifacts include pyrolysis of CaCO_3 in carbonate-rich samples, hydrocarbon retention in mineral grains, and catalytic effect in samples with smectite and illite-rich matrix (Whelan and Thompson-Rizer, 1993; Dembicki, 2009). In fact, pyrolysis of carbonate mineral increases the OI values of samples with high carbonate content, and TOC <2% (Whelan and Thompson-Rizer, 1993). It can be argued that the effect of carbonate pyrolysis seems very low in the Madotz samples, because OI values are invariably low (0–27 mg HC/g rock) for a range of CaCO_3 content between 1.62 and 64.57%. On the other hand, the dominance of smectite and illite matrix that typically reduces the HI, especially in low TOC samples (Whelan and Thompson-Rizer, 1993), could have had effect on the samples. During thermal maturation the HI and TOC are reduced, thus potentially complicating the typification of kerogens that naturally display low HI. However, the Madotz

samples only reach the oil window (see discussion on maturity), hence kerogen determination could not have been much affected by maturity. In general, the results seem to reflect the nature of the kerogen with exception of two of the samples from microfacies (M8), in which the sedimentological data suggest that the organic matter was deposited in suboxic/anoxic environments.

Several parameters from the biomarkers data further indicate that the sample from microfacies M8 (ES-08-46B) accumulated under prevalent reducing conditions in the water column:

- 1) The phytol side of the chlorophyll chain undergoes cleavage and conversion (via phytol) into phytane (Ph) under reducing sediment conditions. Conversely, oxic conditions promote the complete conversion of phytol to pristane (Pr). Thus Pr/Ph ratios between 0.8 and 3 provide information regarding redox conditions in the sediments (Peters et al., 2005b). However, Pr/Ph ratios are also potentially affected by source and maturity. Because Pr/Ph ratios are known to increase with maturity, and the Madotz sample ES-08-46B is clearly within the generative- oil window (see discussion on OM maturation), it is acceptable to invoke reducing conditions as causal factors for its Pr/Ph of 0.88.
- 2) Gammacerane derives from tetrahymanol found in some protozoa, photosynthetic bacteria, marine and fresh water ciliates, among other organisms (Killops & Killops, 2005). Tetrahymanol is mostly biosynthesized in absence of sterols by ciliates that feed on anaerobic bacteria at or below the boundary between oxic and anoxic zones of stratified water columns (Sinninghe Damsté et al., 1995). The presence of relatively high concentration of gammacerane in the Madotz sample ES-08-46B, suggest a stratified water column with anaerobic bacteria in which temporary anoxia was reached.
- 3) The C₃₁₋₃₅ 17 α 22S and 22R homohopanes are used as indicator of redox conditions, in which high C₃₃₋₃₅ homohopanes suggest highly reducing conditions (anoxic) during

deposition (Peters et al., 2005b). If oxygen is available precursor bacteriohopanetetrol is oxidized to a C32 acid followed by loss of carboxyl group to C31 (Peters et al., 2005b). The Madotz sample yielded low C35 homohopane Index (0.04) and a C31C35 homohopane distribution ($C_{31-32} > C_{33-35}$) that suggest reducing conditions were not intense during or immediately after deposition, and eventually oxygen became depleted allowing the preservation of C32 hopane (Demaision et al., 1983).

6.5.4 Elemental Analyses and Redox conditions

Elemental concentrations in fine-grained rocks with mixed terrigenous and biogenic components result from the combined effects of detrital and biogenic fluxes (terrestrial and marine organic matter), and authigenic constituents precipitated close to the water-sediment interface mediated through inorganic and organic reactions driven by Eh-Ph (Sageman and Lyons, 2003).

The transfer of trace metals from biological communities and the seawater to the sediment is conditioned by exposure time (sedimentary rates), rain rates of organic carbon, availability of molecular oxygen, and hydrogen sulfide (Brumsack, 2006; Piper and Calvert, 2009). Specific processes associated with enrichment of trace elements take place during reducing conditions leading to the incorporation of trace metals into sedimentary substrates, including formation of organometallic compounds, authigenic sulfides or hydroxides, and uptake into Fe-sulfides (Algeo and Maynard, 2004; Burdige, 2006; Piper and Calvert, 2009). After deposition/uptake, however, some trace metals and minor elements can be solubilized and remobilized, thus leaving the sediment, or migrating and re-precipitating when oxygen levels change in the bottom and pore waters (Burdige, 2006; Tribovillard et al., 2006). Concentration of individual trace elements and interelemental ratios provide useful proxies to identify levels of bottom-water redox conditions or primary productivity (Piper & Calvert, 2009). In fact, elemental ratios such as $V/(V+Ni)$, V/Cr , Ni/Co and U/Th have been demonstrated as reliable proxies to

estimate paleoredox conditions (Lewan, 1984; Hatch and Leventhal, 1992; Jones and Manning, 1994; Rimmer et al., 2004; Akinlua et al., 2010; Śliwiński et al., 2011). Nonetheless, their use is constrained when the trace element concentrations are in sediments consisting predominantly of terrigenous components.

To better assess the relative trends in elemental fluxes, element abundances are normalized to major dilutants, and element/Al ratios are commonly used. Because aluminum is unaffected by biological or diagenetic processes in nearshore environments, and its abundance varies according to changes in the bulk sedimentation, it is used as the main proxy for clay minerals from fluvial or eolian sources (Sageman & Lyons, 2003; Brumsack, 2006, and others). Furthermore, elemental concentrations can be evaluated relative to average values of a specific lithologic type (e.g. average shale). Here we use enrichment factors that were determined as: $EF = (TE/Al)_{\text{sample}} / (TE/Al)_{\text{average shale}}$ (Brumsack, 2006) using as reference the average elemental concentrations for the average shale by Wedepohl (1971, 1991). Variations in the element concentrations normalized to Al, as well as enrichment factors (EF) were calculated at different levels to show temporal changes in the basin as shown in Table 6-7,

Figure 6-19.

The samples analyzed show that V, Cr, Ni are not enriched relative to the average shale ($EF_V < 0.67$; $EF_{Cr} 0.97-0.75$; $EF_{Ni} < 0.42$). Bivariate plots (Figure 6-16a-c) also reveal strong correlation of V, Cr, Ni with Al, thus suggesting that their concentrations are mostly controlled by terrigenous fluxes rather than by the marine fraction of biogenic debris forming organometallic complexes due to metallation of porphyrins. Thus, temporal variation of these elements and their interelemental ratios are not indicative of changes in the paleoredox conditions in the Madotz section.

U/Th ratios have also been used as redox indicators with values > 0.75 corresponding to oxygen deficient conditions, and 1.25 as the borderline for anoxia (Jones and Manning, 1994). U

and Th show weak and moderate correlation with Al ($R^2=0.2$ and 0.6 , respectively; Figure 6-16g-h), and U/Th ratios yielded values <0.26 for all the samples in subunit 2b. These values suggest that oxygen was consistently available in the water column (Jones and Manning, 1994). However, framboidal pyrite and increased organic matter in samples ES-08-46B and ES-06-48 further document appropriate sulfur concentration in the pore-waters, hence reducing conditions that would allow incorporation of the uranyl ion (UO_2^{2+}) in organic matter of the sediment (Dypvik and Harris, 2001).

Enrichment factor (EF) for Zn, As and Co in the fine-grained sediments at Madotz contain values indicative of depletion, and non-significant enrichment relative to the average shale (EF_{As} , $0.86\text{--}1.88$; EF_{Co} , $0.38\text{--}1.32$; EF_{Zn} , $0.56\text{--}1.11$), Table 6-7. Nevertheless, lithogenic origin as controlling the presence of As and Zn in the samples analyzed seems to be less severe than in the case of V, Cr and Ni, as shown by the moderate correlation values to Al (Figure 6-16e-f and a-c, respectively). Cobalt is largely remobilized with Mn between oxic and sub-oxic pore waters and redeposited in surface oxic sediments (Heggie and Lewis, 1984). Also, Co has strong affinity to terrigenous components, therefore it is often considered an element of limited use as a redox-proxy (Tribovillard et al., 2006). In the case of the Madotz samples Co concentrations are uncorrelated to Al, which argues against strict terrigenous control, therefore, its relative abundance must involve incorporation into sulfides, and/or geochemical pathways similar to Mn, as suggested by the weak but positive correlation between Co/Al and Mn/Al ($R^2=0.24$), (Figure 6-17 f).

As/Al ratios in the Madotz section yielded values of $0.94\text{--}2.07 * 10^{-4}$, average of $1.26 * 10^{-4}$, and $1.36 * 10^{-4}$ in shales and calcareous shales, respectively (Table 6-7). Most of the values are close to the As/Al ratio reported for average shale (As/Al , $1.1 * 10^{-4}$; Wedepohl, 1971, 1991; EF_{As} , $0.86\text{--}1.88$). By comparison, eight Madotz samples show values similar or slightly higher than the average As/Al from the Gulf of California upwelling region ($1.35 * 10^{-4}$; Brumsack,

2006) which appear to be considerably less enriched than other upwelling systems associated with intermittent oxygen depletion. The values obtained in the Madotz section imply less severe oxygen deficient conditions as compared to these systems.

Cobalt solubility in the pore water sediments differs with redox state, and it is released during dissolution of Mn-oxyhydroxides. Co/Al ratios obtained in the Madotz samples yielded values of $0.8\text{--}2.7 \times 10^{-4}$ (average of 1.99×10^{-4} and 1.47×10^{-4} in shales and calcareous shales respectively, Table 6-7), lower than the Co/Al ratio of the average shale (2.1×10^{-4} ; Wedepohl, 1971, 1991). About 8 samples had amounts comparable to - or lower than the average Co/Al recorded in the Peru margin (Co/Al, 1.2×10^{-4} ; Brumsack, 2006) in which leaching of Co associated with Mn- and Fe-oxyhydroxides occurs under sub-oxic conditions (Brumsack, 2006).

Zn/Al values in the studied shale and calcareous shale samples range from $6\text{--}11 \times 10^{-4}$ (average of 10.6×10^{-4} in shales; average of 8.5×10^{-4} calcareous shales); such values are below but close to the average shale (Zn/Al, 11×10^{-4} ; Wedepohl, 1991), and considerably below the average Zn/Al ratios reported in recent upwelling areas associated with high plankton productivity. Low Zn/Al ratios are also compatible with the conditions inferred for the As/Al ratios, which also suggest recycling and/or limited fixation of the element related to environmental redox conditions.

The redox conditions inferred from the elemental results are in agreement with the XRD and petrographic analyses of the facies within the lower part of subunit 2b (Table 6-3), which are characteristically enriched in framboidal pyrite (up to 2.5%) and marcasite. As it is known, sulfidic conditions control pyrite formation (Piper & Calvert, 2009), and metal sulfides are important carrier phases for trace metals such as Co, Zn and As, among other elements (Huerta-Diaz and Morse, 1992; Burdige, 2006; Tribovillard et al., 2006). Thus, the results confirm that sulfate reduction took place in the sediment pore waters, although other proxies such as

lithofacies and bioturbation index indicate that bottom waters were either fully oxygenated or did not reach severe levels of oxygen deficiency.

The low TOC values, the kerogen type (kerogen type IV indicative of highly degraded OM), and the low correlation of the Al normalized trace metals to TOC (trace metal/Al vs TOC), further document that the non detritic fraction of these elements is concentrated in sulfides rather than in OM (as organometallic complexes). Thus, small variations in the As/Al, Co/Al, and to a lesser degree the Zn/Al ratios, invoke processes related to various factors such as formation and trapping of trace metals within the sulfide phases, the intensity of sulfide conditions in the pore waters, as well as the ease of the different trace metals to incorporate into pyrite. In fact, As is preferentially incorporated over Co and Zn, and thus shows the highest enrichment factors (Huerta-Diaz & Morse, 1992).

Barium enrichment factors (EF_{Ba}) in unit 2b range from 0.6 to 1 (Ba/Al, $39-69 \times 10^{-4}$ in calcareous claystones and shales; Ba/Al $51-71 \times 10^{-4}$ in marlstones and limestones). Only three individual levels of marlstone and calcareous shale (beds ES-06-26, 30 and 34) show Ba/Al values in the order of the average shale (Ba/Al, 66×10^{-4} ; Brumsack, 2006). The Ba signal is partially controlled by terrigenous inputs as suggested by the moderate correlation of Ba with Al ($R^2=0.74$) in the samples from Madotz.). Ba occurs in sediments in detritic plagioclase and in the form of barite ($BaSO_4$) precipitated in water column or in the pore waters where it mostly develops through phytoplankton decay (Tribovillard et al., 2006; Griffith and Paytan, 2012). Barite is stable during sulfate seawater concentrations and is prone to enrichment at low sedimentary rates, but is sensitive to alteration under reducing conditions when Ba is mobilized. Mobilized Ba reprecipitate as barite or Ba-rich oxyhydroxide within sediments with sulfate-rich pore waters at the oxic/anoxic redox boundary (Tribovillard, et al., 2006; Griffith & Paytan, 2012). Reprecipitation of barite can occur also within suboxic pore waters if sulfate is still available (McManus et al., 1998). Thus, Ba is considered to have limited application as a

paleoproductivity proxy in sediments characterized by intense sulfate bacterial reduction such as black shales (Sageman & Lyons, 2003; Brumsack, 2006; Tribovillard, et al., 2006). Ba/Al values in the shale samples are consistently below values reported in upwelling locations and anoxic basins (Böning et al., 2004; Brumsack, 2006), suggesting lower primary productivity in the studied section relative to upwelling settings and restricted basins. Because Ba has a behavior similar to Mn, relatively high values of Ba/Al are interpreted here as a relative indicator to further corroborate an oxygenated sediment-water interface, and low Ba/Al values are used as indicator of sulfidic conditions within the pore waters.

The negative correlation of Mn to Al ($R^2=0.13$) in the Madotz samples is in agreement with the high correlation of Mn/Al to Ca ($R^2=0.79$; Figure 6-17c). Such correlation suggests that manganese is mostly associated with the carbonate fraction of the sediment, hence implying the precipitation of Mn-carbonates (rhodochrosite, MnCO_3) and mixed Mn-and-Ca carbonates (kutnahorite, manganoan calcite) in suboxic pore waters. This interpretation is based on the behavior of Mn which becomes mobile under reducing conditions (Mn^{2+}), while it precipitates as Mn-oxyhydroxides (MnO_2 , MnOOH) under oxidizing conditions ($E_h > 500\text{mV}$). Thus, in oxic environments with reducing pore waters, rapid upward remobilization of Mn^{2+} induces Mn to reprecipitate as oxides at the redox boundary. Supersaturation with respect to Mn carbonate in suboxic or anoxic pore waters leads to Mn carbonate phases as dispersive precipitate into the deeper sediment, some distance away from the Mn oxide peak. Such “pumping” effect does not develop in anoxic waters because Mn-oxyhydroxides do not precipitate in the sediment, and reduced Mn^{2+} is recycled or lost to the water column (Calvert and Pedersen, 1993; Sageman and Lyons, 2003; Burdige, 2006 and references therein).

The Mn/Al values ($11\text{--}35 * 10^{-4}$) in the Madotz samples are lower than the average shale ($\text{Mn/Al}, 96 * 10^{-4}$; Wedepohl, 1971, 1991; Table 6-7) and result in low enrichment factors ($EF_{\text{Mn}}, 0.13\text{--}0.28$) that suggest episodic oxygen depletion. Also, the range of Mn/Al values ($11\text{--}35 *$

10^4) in the shales, claystones and marlstones of subunit 2b is lower than the average ratios for sediments in the Gulf of California (Mn/Al , $41 \cdot 10^{-4}$; Brumsack, 2006) and the Peru margin upwelling areas (Mn/Al , $52 \cdot 10^{-4}$; Brumsack, 2006), where Mn is remobilized under reducing conditions related to the oxygen minimum zone.

In order to clarify these apparent discrepancies of Mn as a proxy to redox conditions in the Madotz section, one may consider multiple scenarios of its presence in the sediments: taking as a main reference the concentrations of Mn, but all of them represent intermediate situations between the following cases (

Figure 6-19):

- 1) Bed ES-06-24 (Microfacies M6) contains the highest Mn/Al values of the series, as well as high Zn/Al, intermediate Ba/Al, and low As/Al. This level includes common benthic faunas, bioturbation, and low TOC. The components of this microfacies clearly indicate an oxygenated water/sediment interface, and intermediate and low Ba/Al and As/Al do confirm that sulfidic conditions in the pore water were not intense. Because conditions were mostly oxic, this level with low total Ba concentration may also be related to reduced productivity compared to corresponding levels of shales. Again, Mn can be associated with formation of authigenic oxyhydroxides (MnO_2 , MnOOH) in oxic pore waters.
- 2) Bed ES-06-30 (Microfacies M6) contains low Mn/Al, very low Co/Al, As/Al, Zn/Al and U/Al, and high Ba/Al (Fig. 6–19; Table 6–7). This bed consists of abundant fossils, it is bioturbated and yielded low TOC values. As discussed above, this microfacies (M6) is indicative of oxygenated conditions at the water/sediment interface, despite the Mn/Al that could suggest reducing conditions and even loss of Mn during short lasting disoxic episodes in the bottom waters. In fact, dispersive pyrite may be misleading, because low Co/Al, As/Al, Zn/Al and Ba/Al attest that sulfidic conditions were not dominant in the pore waters. Thus, assuming brief periodic dysoxia, the Ba/Al can be related to precipitation of barite at the

- redox boundary when re-oxygenation took place, whereas U/Al minimum may reflect remobilization of U as the oxygenation fronts advanced down into the sediment column during more oxic conditions (Tribovillard, et al., 2006).
- 3) Bed ES-06-34, 36, 26 (Microfacies M6) shows moderate Mn/Al, Ba/Al, and Zn/Al, also moderate U/Al and P, relatively high Co/Al, but highly variable As/Al. As in previous levels they also include common benthic faunas and are bioturbated, indicating oxygenated conditions at the water/sediment interface. Nonetheless, some disseminated pyrite, and the As/Al indicate plausible sulfate reduction in pore waters was occasionally/locally involved. Indeed, a marlstone bed (ES-06-25; Microfacies M6) with moderate Mn/Al and Ba/Al contains pyrite nodules certainly linked to localized sulfidic condition in the pore waters.
 - 4) The clay-shale interval (36–37.8 m; ES-06-44, 45, 46b, 46, Microfacies M8) is also of interest as it is unique in its characteristics as previously described. This interval with highest TOC is very poor in benthic faunas, and yielded the lowest Mn/Al ratio (Figure 6–19; Table 6–7) of the section. As discussed earlier, the low Mn/Al ratios are consistent with Mn solubilization and remobilization as suboxia/anoxia developed in bottom waters and enhanced carbon sequestration. Sulfidic conditions in pore waters are supported by the presence of up to 4% pyrite and very low Ba/Al values, however, As/Al values are close to the average shale. Relatively high Zn/Al ratios could be partially influenced by the higher accumulation of OM in the sediments. Low Co/Al also suggests its recycling with Mn oxides and carbonates between oxic and suboxic pore waters (Brumsack, 2006).
 - 5) Beds at different levels (ES-06-28, Microfacies M6; ES-06-37, 43, 47, 49, Microfacies M7) have low Mn/Al ratios, generally low to moderate Ba/Al, moderate to high As/Al, Co/Al, Zn/Al. These beds are pyritic, but also contain benthic faunas (low abundance in some of the beds), they are bioturbated, and with modest amount of OM. As in previous cases, they further illustrate a sediment column with episodic dysoxic water/sediment interface, and

highly reducing pore waters, which allowed some solubilization and recycling of Mn and Ba. Episodic development of some degree of oxygenated sediment/water interface allowed biotic activity and bioturbation. Sulfidic pore waters led to pyrite formation and relative increase in As/Al, Co/Al, and Zn/Al. Sample ES-06-37 with intermediate Ba/Al would suggest incomplete recycling of barite formed in the redox boundary during periods of oxygenation. Other beds from Microfacies 5 and 6 (Figure 6–9, Table 6–1) yielded similarly low Mn/Al and Ba/Al, but moderate to low Zn/Al, As/Al, Co/Al (Figure 6–19, Table 6–7). They contain common benthic faunas, and are interpreted to represent less sulfidic conditions in the pore waters.

6.5.5 Terrigenous Inputs and Paleoclimate Evidence

Lithophile elements constitute about 93 percent of the earth's crust, and they constitute the major components of terrigenous materials. Hence, bulk mineralogical and chemical composition of sediments provide critical information on the provenance of the terrigenous materials produced by the interaction of tectonism and weathering related to climate, mitigated by the effects of different transport processes into the basins. The net particulate flux in order of abundance of the predominant lithophile components from modern fluvial sources are Si, Al, Fe, Ca, K, Mg, Na, Ti, P, Mn, and Ba (Sageman & Lyons, 2003). Except for Al and Ti, biological and diagenetic overprinting processes often modify major element abundances as presented in the previous sections.

Studies of clay mineral composition of Mesozoic and Tertiary mudstones indicate that they mainly reflect a combination of weathering, climate, relief and source rocks in the continent. Moreover, clay mineral assemblages can be altered by differential transport in suspension, differential sensitivity to changes in pH from fresh to saline water, and can experience further mineralogical alteration during burial diagenesis (Potter et al., 2004; Meunier, 2005). Thus, paleoclimatic interpretation of clay minerals assemblages requires the use of data where the

effects of clay transport and diagenesis did not obliterate the signal of conditions of their provenance.

XRD and petrographic analyses reveal that in the Madotz section Si is present partly as clay minerals, silt-size quartz matrix, and silt-size particles agglutinated in exoskeleton of orbitolinids. Combined SEM/EDS, and XRD results indicate that feldspars are a negligible component of the fine terrigenous fraction in the studied samples. Thus, concentrations of Al, K and Mg (Table 6-7, Figure 6-18) reflect true abundance of clay minerals (illite, kaolinite, smectite, and chlorite), and their pertinent increase in the claystones, clay-shales and some calcareous claystones. In fact, decreases in Si, K, Fe, Mg, Ti and Al are usually associated with levels richer in carbonate (e.g. the intervals from 30.1 to 30.65 m, and from 33.4 to 33.9 m); attesting temporary reduction of siliciclastic inputs.

Results of the clay mineralogy indicate that illite is the dominant component in most of the samples from the Madotz section, and its abundance is inversely correlated to the abundance of smectite (Table 6-4). This correlation suggests that illite and illite/smectite layers are a diagenetic product formed at expenses of smectite (Hower et al., 1976) rather than derived from acid soils subjected to repeated wetting and drying though K fixation in smectite (Huggett, 2005). Illite and chlorite can also develop in soils dominated by mechanical weathering in hot and dry climates (Chamley, 1989), which does not seem to be consistent with the provenance of the clays in the Madotz sediments, because chlorite is negatively correlated to illite; illite is negatively correlated to carbonate; and, chlorite is totally uncorrelated to carbonate.

The interpretation proposed is the effects of burial, lithostatic pressure with depth, temperature and time, smectite (with addition of potassium) gradually transformed into illite, with release of silica (quartz) and/or chlorite (Hower et al., 1976; Weaver, 1989; Moore and Reynolds, 1997). Mixed layers illite and smectite form randomly ordered stacking sequences (R0 I/S) during low stages of diagenesis (<50% Illite, <0.6 Ro; Kübler and Jaboyedoff, 2000); as diagenesis

increases (55–65% illite, ~10000 feet) so does illite crystals and the structure is replaced by ordered mixed layers of illite and smectite known as R1 I/S structure.

On the other hand, the following characteristics of the sediments also indicate that the clay mineral assemblages still retain part of the paleoclimate signal despite diagenetic transformation from smectite to illite:

- 1) Thermal maturation of the organic matter inferred from the Rock-Eval pyrolysis ($T_{\max}$ 319°–446°C, mean 426°C, Table 6–2, Figure 6–11), and different biomarker indicators, reveal a low to medium degree of thermal diagenesis, with most of the data suggesting the early oil, and peak oil stages, which approximately correspond to the beginning of the transition of R 0.5 to R1 illite/smectite layers, or the early stage 3 of Kübler and Jaboyedoff (2000).
- 2) Clay-size feldspar grains are observed in the SEM/EDS, although they were not detected in the bulk XRD analyses. This implies that K released from feldspar was not a factor in the conversion of smectite to illite, and the conversion process was unfinished, so our assemblages are complete diagenetic product.
- 3) Variations in the relative percentages of kaolinite and smectite are in agreement with the general lithologic types and their main vertical distribution, as smectite increases in carbonate dominated intervals, while kaolinite is prevalent in mudrock intervals, which suggests that their variation is also controlled by weathering of the original materials rather than by diagenesis.

Thus, kaolinite and smectite are here interpreted as products of soil weathering under different and contrasting climatic regime, humid versus dry, respectively (Weaver, 1989; Wilson, 1999; Sheldon & Tabor, 2009), at subtropical regions (basque cantabrian region ~30°N in (Torsvik et al., 2002), thus increase in the kaolinite/smectite ratio is indicative of a more humid climate on land.

In the Madotz sediments the transition between terrigenous-dominated unit 1 and carbonate-dominated subunit 2a reveals a sharp decrease in the kaolinite/smectite ratio ($K/S > 1$), while there is an increase in the smectite/illite ratios ($S/I < 1$) concomitant with an overall decrease in clay and quartz, and an increase in carbonate (Fig. 6–12; Fig. 5 in Gaona-Narvaez et al., 2013). Such changes are interpreted as a transition from a prevailing humid regime at time of deposition of unit 1, to drier regime with low terrigenous inputs that allowed carbonate production. Subunit 2a is characterized by very low kaolinite/smectite ratios (< 1), and very low total content of clays.

The lower part of subunit 2b, composed of calcareous claystones, marlstones and shales assigned to microfacies M5, M6, M7, and M8, is characterized by a sharp increase in the kaolinite/smectite ratios to values above 1 (7–9). There is simultaneous reduction in carbonate (both TIC and XRD measured), and increase in the total content of clays and quartz relative to subunit 2a. Such change in the bulk mineralogical composition is interpreted as resulting from increasing siliciclastic fluxes related to a switch toward more humid regional climate regime. The increase in kaolinite, however, is less evident from the kaolinite/chlorite, and the kaolinite/illite ratios, and perhaps can be explained as an effect of sampling bias of subunit 2a collected more in beds with higher siliciclastic component (sample with microfacies M2, M4, M5) rather than in the typical calcareous lithology of the unit (microfacies M3, e.g. ES-06-17).

In contrast, the upper part of subunit 2b includes lower and variable kaolinite/smectite ratios (0–3.63), as well as a small increase in the smectite/illite ratios (0.04–0.87) relative to the lower part of the subunit (Figure 6–13, Table 6–14). These changes are concomitant with an increase in carbonate (visible in the TIC and XRD) and an overall decrease in clay. This segment of the section is interpreted as a record of a relative decrease in the volume of detrital inputs to the basin, as well as changes in weathering on land, as suggested by the increase in the contents of smectite relative to kaolinite and illite. The data are limited for the lower part of subunit 2c, but the few samples analyzed show clay mineral relative abundances similar to the ranges obtained

for the upper part of subunit 2b kaolinite/smectite ratios are close to 1 (0.72–0.77), with intermediate smectite/illite values (0.19–0.32). However clay mineral ratios in the lower part of subunit 2c (Figure 6–13, Table 6–14) are less variable than those in the infrajacent unit, and are concurrent with an increase in carbonate and decrease in total clay. These mineralogical changes document a slow normalization of the carbonate production under dry conditions with severely reduced input of siliciclastics to the basin.

6.5.6 Geochemical Evidence for Nutrient Content at Madotz

In an effort to shed light on paleoproductivity levels in the Madotz section, the concentrations of phosphorous were obtained from samples within the subunit 2b which correlates with the highest record of siliciclastic and OM accumulation, and corresponds with interval that includes OAE-1a, as demonstrated by carbon isotope chemostratigraphy (Gaona-Narvaez, 2013a). To estimate the productivity level, available P is the most dependable evidence since Ba has limited application as a paleoproductivity proxy in sediments characterized by intense sulfate bacterial reduction such a black shales (Sageman & Lyons, 2003; Brumsack, 2006; Tribovillard, et al., 2006). Phosphorus is delivered to the ocean from terrigenous fluxes or from upwelling. Occurring as phosphate ion $(\text{PO}_4)^{3-}$ phosphorus is an important biolimiting nutrient; hence, its availability is critical for sustained productivity of primary producers that are at the origin of most of the organic matter in the marine environment. In the case of the Madotz section, the main producers would have been algae, protists (e.g. dinoflagellates), and cyanobacteria as supported by the abundance of *n*-alkanes and dinosteroids reported previously.

Phosphorous (P_2O_5) values in the samples analyzed range from 0.07 to 0.6% (343–2893 ppm), TOC/P ratios between 0.6 and 20, and enrichment factors (EF) with respect to the average shale between 0.28 and 3.2. By comparison with other Tethyan sites, the values of total P in stages C4 and C5 of OAE-1a at Madotz (see Figure 4.5, herein) are higher than those reported for

the Lower Aptian orbitolinid-rich Rawil Member, Swiss Helvetic Alps (maximum of 313 ppm; Stein et al., 2012a).

The clay shale interval with the peak of TOC in the Madotz section (36–37.8 m; TOC=0.4–1.28%) shows P concentrations below the average shale (EF_p , 0.36–0.54; TOC/P, 7–20). The interval shows evidence from the biomarkers and microfacies (M7 and M8) that suboxic to anoxic conditions were prevalent. Since these samples contain 3 to 4% pyrite, low Mn, and low Ba, the relatively low P concentrations (both total and normalized to Al) can be attributed to possible remobilization of P during suboxic to anoxic conditions in both the pore and bottom waters.

6.5.7 Evidence for Sea Level Changes in the Madotz Section

As shown in Figure 6–20, at least six full, and two partial short-term regressive-transgressive (T-R) cycles are interpreted within the studied 62 m section at Madotz. based on on integrated temporal microfacies distribution, stacking pattern and sedimentology of the outcrop. The short-term T-R cycles are grouped according to their depositional makeup transgressive or regressive tendency and interpreted together with meaningful surfaces associated with compositional trends reflecting relative sea level change. The local sequence stratigraphy of Madotz is also compared to the long-term (third order) T-R cycles of Hardenbol et al. (1998) and Gradstein et al. (2004) actualized by Ogg and Ogg (2008); Figures 6–20 and 6–21.

6.5.7.1 *Unit 1 and Subunit 2a.*

The lithologic change from the biotubated claystones of Unit 1 to the pure carbonate shoal facies of Subunit 2a, is interpreted as the result of severe reduction of local terrigenous input that allowed the development of the carbonate factory and formation of shoals on the ramp/platform (distal expression : Microfacies M3, M4). The deposit also involves a minor sequence boundary in the lowest part of subunit 2a represented by the contact between beds containing microfacies associations 2 and 3. Subunit 2a encloses 2.5 short-term T-R cycles

interpreted from textural changes of packed developing into sparse biocalcitrudites in microfacies M3.

Figure 6-20 Summary of the sedimentary environments and sequence stratigraphy interpreted for the Madotz section. M1-M10: described microfacies. Textures: M, mudstone; W, wackestone; P, packstone. LST: lowstand system tract; TST, transgressive system tract; HST, highstand system tract; SB: sequence boundary; TS, transgressive surface; MFS, maximum flooding surface.

Evidence for surfaces of subaerial exposure is not clear; thus an oxidation crust at the top of subunit 2a is interpreted as a transgressive surface. Subunit 2a is therefore interpreted as the lowstand systems tract (LST) of a third order sequence.

6.5.7.2 Subunit 2b and 2c

The drastic change from pure carbonate facies of Subunit 2a to the low diversity, orbitolinid-rich mixed carbonate/terrigenous facies of subunit 2b, is interpreted as a result of increased fine terrigenous input concurrent with relative sea level rise thus producing bioclastic and fine terrigenous materials below the fair-weather wave base (FWB) and above the storm wave base (SWB) typical of microfacies M5, M6, and M7. Short term T-R cycles in subunit 2b are determined from fossil associations and textural changes, with orbitolinid-dominated facies (M5) developed in slightly shallower environments than orbitolinid poor/absent facies (M6, M8). Peaks of aluminum, interpreted as related to clay abundance, are also considered to determine the flooding surface between cycles.

Short-term T-R cycles show a vertical progression toward more distal environments through subunit 2a and the lower part of subunit 2b. The reversal from this transgressive tendency toward a regressive tendency takes place 37 m above the base of the section and marks the maximum flooding surface (MFS) of a third order sequence.

The MFS coincides with the thickest level of claystones and shales of subunit 2b (1.8m) and the maximal development of microfacies M7 and M8. The MFS is characterized by overall low content of silt-size quartz, rare benthic foraminifera and benthic macro-invertebrate faunas, common calcispheres and ostracods, common disseminated pyrite, low bioturbation index, as well as the main peak of TOC in the section (0.5-1.27%). These features would indicate a quiet distal bottom subject to seasonal depletion in the oxygen levels at the water/sediment interface.

The beginning of highstand systems tract (HST) of a third order sequence correlates with the upper part of subunit 2b and the lower portion of subunit 2c.

Figure 6-21 Sequence stratigraphic framework of the Madotz section compared to the Tethyan stratigraphic framework

The HST in the section is characterized by increasing thickness of the short term T-R cycles, gradual reduction of the siliciclastic input, disappearance of off-shore and platform-margin orbitolinid-dominated facies (microfacies M5, M4), and expansion of a carbonate platform facies (microfacies M9, M10). Assigning part of the orbitolinid-rich episodes of subunit 2b to a transgressive episode is in agreement with previous authors (Pittet et al., 2002; Bachmann and Hirsch, 2006; Bovel-Arnal, 2009; Embry et al., 2010) who determined that orbitolinid episodes were common in the context of enhanced supply of nutrients and terrigenous materials due to increased rainfall, weathering, and reworking of platform muds during periods of transgression. However, at Madotz, orbitolinids episodes extended into the first stages of the regressive portion of the long-term cycle (cf. Hardenbol et al., 1998), or the beginning of the HST (Figure 6–20). The increased frequency observed in the short term T-R cycles of subunit 2b synchronous with OAE-1a (Gaona-Narvaez et al., 2013), is interpreted as a result of reduced accommodation in distal environments during the late stages of the transgressive systems tract (TST) and earliest stages of HST (Figure 6–20).

As shown in Figure 6–21 there is only partial agreement between the sea level changes interpreted for the Madotz sequence compared to the longterm T-R cycles of Haq et al. (1987, 1988), Hardenbol et al. (1998), and Ogg and Ogg (2008). The Madotz section includes a minor sequence boundary and a LST associated with carbonate deposits of subunit 2a, in contrast to the continuous transgressive trend through *Deshayesites forbesi* Zone proposed by Ogg and Ogg, (2008). Such minor sequence boundary at Madotz was probably driven by local physiographic factors related to tectonics. Other difference with Ogg and Ogg (2008) is the stratigraphic position of the MFS that coincides with the peak of OAE-1a. The MFS identified at Madotz is concomitant with the maximal expression of facies indicative of oxygen-depleted bottoms (Microfacies M8), and possibly coincides with the MFS between sequences boundaries Apt3 and Apt4 that, according to Haq et al. (1987; 1988) and Hardenbol et al. (1998), is placed in the upper

part of *Deshayesites forbesi* zones rather than at the boundary between *Deshayesites forbesi* and *Deshayesites deshayesi* Zones as proposed by Ogg and Ogg (2008). Of interest for correlation with the Madotz section is that in the Maestrat Basin a MFS is also described in the upper part of the *Deshayesites forbesi* zone (Bover Arnal et al., 2009). The upper part of subunit 2b and the basal portion of subunit 2c at Madotz, coincident with the beginning of the HST in the section, also correlate well with the stratigraphic events reported in the Maestrat basin (Haq et al., 1987, 1988, Hardenbol et al., 1998; Bover-Arnal et al., 2009).

6.5.8 Temporal Environmental Evolution of the Madotz Section in the Context of OEA-1a

6.5.8.1 *The Pre-OAE-1a Phase (Figure 6–22)*

The different parameters analyzed as proxies discussed in this study permit the following reconstruction of the temporal evolution of the depositional environment recorded in sediments of the Madotz section, as illustrated in Figure 6–22:

The initial phase prior to the onset of conditions precursors to OAE-1a includes the predominately basal siliciclastic interval represented at Madotz by Unit 1, and probably also the subsequent episode of carbonate deposition represented by subunit 2a correlative with biostratigraphic levels older than the previously assigned *Deshayesites deshayesi* zone. The basal Unit 1 (microfacies M1) is coeval with $\delta^{13}\text{C}$ stage C2 (Figure 6–13) and developed in open shallow-marine conditions. The siliciclastic Unit 1 at Madotz and the Errenaga Fm. in the Aralar (Duvernois et al., 1972; García-Mondéjar et al., 2009) both attest to prevailing humid climates at that time as demonstrated also by clay minerals studies of the northern margin of the Tethys (Godet et al., 2008). The detailed clay study indicates three intervals of increased kaolinitic input from the latest Barremian to the earliest Aptian prior to the onset of conditions associated with OAE-1a (*D. oglanlensis* to *D. weissii* zones). On a global scale, the lowest Aptian deposits synchronous with the C-isotope stage C2, synchronize as well with a period of increased supply of non-radiogenic Os, inducing a negative excursion of marine $^{187}\text{Os}/^{188}\text{Os}$ indicative of increased

terrigenous fluxes from weathering of continental crustal rocks (Tejada et al., 2009).

The sedimentary record at Madotz demonstrates a switch from terrigenous sedimentation (Unit 1) to pure carbonate (subunit 2a) that predates OAE-1a. The shallowing of the environment is indicated by the progression from claystones (microfacies M1) and sparse biocalcarenites, both indicative of low energy conditions (Microfacies M2), to packed calcirudites indicative of relatively high energy shoals (Microfacies M3). High diversity and composition of the fossil assemblages in the carbonate facies, including common corals, calcareous algae and minor rudistid bivalves, suggest oligotrophic conditions (photozoan association of Mutti and Hallock, 2003). Two very short punctual events of orbitolinid facies (Microfacies M4) also occur in coincidence with slight increases in siliciclastic input. All the facies types present at this stage are indicative of fully oxygenated conditions within the photic zone, with most likely extensive recycling of OM leading to very low TOC. The episode of development of carbonates of subunit 2a may coincide with a period of reduction in weathering rates immediately preceding the onset of OAE-1a (Tejada et al., 2009).

Mixed carbonate-siliciclastic facies of subunit 2b at Madotz are limited to the southwest part of the Aralar mountains, and are equivalent to siliciclastic facies that develop toward the northwest near Beloki and Igaratza (Duvernois et al., 1972; García-Mondéjar et al., 2009). This spatial facies change thus confirm that carbonates in the Madotz area represent marginal facies of an early platform/ramp toward the south.

6.5.8.2 The OAE-1a Phase (Figure 6–22)

The sedimentary sequence of subunit 2b concomitant with OAE-1a phase at Madotz is clearly recognized by its isotopic signals correlated with segments C4 to C6 and is coeval with the upper part of the *Deshayesites forbesi* Zone (Gaona-Narvaez et al., 2013). However, the interval associated with negative carbon isotope excursion C3 that characterizes the beginning of OAE-1a, is uncertain. The drastic reduction of carbonate content in the section from underlying

lithologic unit 2a to 2b would suggest that C3 excursion is located in the lowest 3.5m of lithologic subunit 2b. It is estimated a thickness of 79 to 92 cm for the isotopic interval C3 in the studied section assuming sedimentation rates between 1.8 to 2.09 cm/kyr (Gaona-Narvaez et al., 2013) during the 44 kyr (Li et al., 2008).

Figure 6-22 Inferred evolution of sedimentary environments for the Madotz section. M1-M10 are microfacies described in the text; C2-C7, stable carbon isotope stages by Menegatti et al. (1998); FWWB, fair weather wave base; SWB, storm weather wave base.

Lithologic variations observed within the OAE-1a interval at Madotz are as follows: C-isotope segments C4 and C5 (~ 900 to 930 kyr, Li et al., 2008) are characterized by abundant orbitolinid-rich limestones, marlstones and claystones (microfacies M4, M5), and interbeds of facies with poor/absent orbitolinids (microfacies M6, M7, M8), some of which show low bioturbation index, poor fossil content (few ostracods and calcispheres, rare/absent benthic foraminifers), pyrite and higher TOC (microfacies M8). These sediments accumulated in an outer platform/ramp to proximal platform slope setting, between the fair-weather wave base and above the storm wave base. As discussed before, some of these levels developed under periodic

suboxic conditions (microfacies M8), which recurred within at least three of a total of 7.5 T-R short term cycles identified during OAE-1a. The thickest level with prevalent facies indicative of suboxic conditions is at ~36m above the base of the section and includes the MFS of a third order sequence. The estimated duration for this prevalent suboxic interval is 95.23 to 120 ky (Gaona-Narvaez et al., 2013). The MFS associated with OAE-1a recorded in the Madotz sequence may be of regional significance because similar features are reported in the same interval in the Maestrat Basin (Bover-Arnal et al., 2009, 2011), and the Galve Su-Basin, NE Spain (Embry et al., 2010). However, a discrepancy exists in the timing of the Galve Sub-Basin event that is further discussed in Chapter 4 (Gaona-Narvaez et al., 2013).

The last stratigraphic equivalent to OAE-1a interval at Madotz, lies within $\delta^{13}\text{C}_{\text{org}}$ stage C6 (~300 to 330 kyr, Li et al., 2008), and correlates with the upper part of subunit 2b. As previously described, these sediments show progression from shallow muddy environments dominated by orbitolinids (Microfacies M5), to carbonate environments adjacent to orbitolinid shoals (Microfacies M4). These environments developed during $\delta^{13}\text{C}_{\text{org}}$ stage C6 were fully oxygenated, with high recycling of organic matter, with higher energy conditions and shallower than those present at Madotz at the time of $\delta^{13}\text{C}_{\text{org}}$ stages C4 and C5. C-isotope stage C6 is concurrent with the early regressive phase of the long term T-R cycle or the early HST of a third order sequence.

6.5.8.2.1 Meaning of orbitolinid facies during OAE-1a

Orbitolinid-rich facies developed at different times in Lower Cretaceous series from intertidal to carbonate slope settings (Vilas et al., 1995; Hughes, 1998; Pittet et al., 2002; Bachmann and Hirsch, 2006; Bover-Arnal et al., 2009; Masse et al., 2009; Embry et al., 2010). Orbitolinid-rich episodes also represent major breaks in the temporal and spatial evolution of carbonate platforms (Weissert et al., 1998; Föllmi and Gainon, 2008; Masse et al., 2009), and are interpreted as the transitional stage from platform to ramp configuration (Masse et al., 2009).

These episodes have been related to enhanced supply of nutrients and terrigenous materials under more humid climates and/or reworking of platform muds during periods of transgression (Pittet et al., 2002; Bachmann and Hirsch, 2006; Bover-Arnal et al., 2009; Embry et al., 2010).

Pittet et al. (2002) and Embry et al., (2010) further discussed discoidal orbitolinids ecosystems as related to their morphological adaptation to poorly illuminated clay-rich environments, their possible symbiosis with zooxanthellae, and the determinant ecological strategies for their abundance in clay-rich and nutrient-rich environments.

As presented in preceeding paragraphs, the combined mineralogical and geochemical record at Madotz at the time of OAE-1a support the relation between orbitolinid-rich episodes and periods of increased supply of siliciclastics in a transgressive and early highstand context. Orbitolinid assemblages at Madotz consist of various heterotrophs, including echinoderms, bivalves, brachiopods, foraminifera (heterozoan assemblages cf. James, 1997), and organisms with generalist trophic strategies (Vilas et al., 1995; Pittet et al., 2002; Embry et al., 2010), they show low diversity, and high dominance. These characteristics can be typical of tropical and subtropical assemblages in mesotrophic and eutrophic environments (Brasier, 1995; Mutti and Hallock, 2003). Requirements conducive to development of such environments were met at Madotz, as values of total phosphorous (P, 343–2893 ppm; P_2O_5 0.078–0.66%) in subunit 2b (stages C4 and C5 of OAE-1a in the section) are comparable to values reported for the Lower Aptian orbitolinid-rich Rawil Member (P maximum, 313 ppm; Stein et al., 2011). Also, orbitolinid-bearing microfacies M5 and M6 show P-enrichment factors (EF) with respect to the average shale between 0.28 and 3.2, which is attributed to increase flux of nutrients associated with terrigenous that lead to increased primary productivity at the time of OAE-1a. Coeval sedimentological/paleoecological changes related to increased nutrient influx are reported in many other locations and sedimentary settings (Pittet et al., 2002; Immenhauser et al., 2005; Huck et al., 2010; Rameil et al., 2010; Erba and Tremolada, 2004; Dumitrescu and Brassell, 2005;

Luciani et al., 2006; Heldt et al., 2008; Tejada et al., 2009).

6.5.8.3 The post- OAE-1a phase (Figure 6–22)

The pure carbonate facies at the base of subunit 2c in the Madotz section coincide with the lowest part of the $\delta^{13}\text{C}_{\text{org}}$ interval C7 (Figure 6–13) and the post-OAE-1a phase (Gaona-Narvaez et al., 2013). The environment at the site returned to oligotrophic conditions with high-diversity assemblages including abundant miliolids (microfacies M9), succeeded by low-diversity assemblages dominated with requienid rudists (M10). The faunal assemblages associated with these microfacies suggest subtidal environments of an inner carbonate platform in the Madotz and the Irugatza sections, 11.5 km NW of Madotz (Millán et al., 2009). By contrast, the Sarastarri Fm. accumulated mixed terrigenous and carbonate materials of tidal origin, or “Calcarenitas de Agaotz” (Lertxundi and Garcia-Mondejar, 1997).

6.6 Conclusions

The proxies used in this study of the Madotz section (Navarra, Spain) provide a detailed evidence of paleoenvironmental conditions in the Lower Aptian sequence previously named unit 1, subunit 2a, subunit 2b, and subunit 2c (Duvernois et al., 1972; Cherchi and Schroeder, 1998). These units are coincident with the time interval before, during, and subsequent to the global event known as Oceanic Anoxic Event 1a (OAE-1a).

Based on ammonite taxa and chemostratigraphy, the lowermost part of the section, or siliciclastic Unit 1 (0 to 3 m), is now placed at the biochronologic level of the *Deshayesites weissi* zone (Gaona et al., 2013), or an older level than the previously assigned *Deshayesites deshaysi* zone (Cherchi and Schroeder, 1998; and others). Unit 1 corresponds to $\delta^{13}\text{C}$ stage C2 (Menegatti et al., 1998) or the time preceding the global Lower Aptian Oceanic Anoxic Event 1a, and developed in open, shallow-marine conditions, under prevailing humid climates as recorded by increased kaolinitic clay, consistent with increased supply of non-radiogenic Os, and a negative excursion of marine $^{187}\text{Os}/^{188}\text{Os}$ (Tejada et al., 2009).

Subunit 2a (3 to 26.6 m) also predated OAE-1a and is a nearly pure carbonate platform margin deposit (TIC>90 wt%), thus indicating drastic changes in environmental conditions from infrajacent siliciclastic Unit 1. It is characterized by Urganian facies, low in TOC, with diverse photozoan assemblages, indicative of well-oxygenated, relatively high energy shoals and oligotrophic conditions. Two minor interbeds of orbitolinid facies coincide with slight increases in siliciclastics.

Subunit 2b (26.6 to 49.2 m) documents a period of significant environmental changes characterized by extensive mixed carbonate and terrigenous facies within the time interval coeval with of OAE-1a and $\delta^{13}\text{C}$ stages C4 to C6, and the *Deshayesites forbesi* ammonite Zone (Reboulet et al, 2012; Gaona-Narvaez et al., 2013). Lithologic types include abundant muddy limestones, marlstones, and claystones, as well as clay-shale interbeds with low bioturbation index, pyrite and higher TOC. This interval is restricted to $\delta^{13}\text{C}$ stages C4 and C5. Subunit 2b developed in outer platform/ramp to proximal platform slope settings subject to recurrent suboxic conditions at least for 95.2 to 120 ky. Most of the time, conditions were favorable to heterozoan assemblages dominated by orbitolinid or other agglutinated foraminifera (*Choffatella decipiens* and *Pseudocyclammina hedbergi*) in slightly less energetic oxic bottom, between the fair weather and the storm wave bases. The most prevalent development of suboxic facies (~36 m) highlights the MFS and early HST of a third order sequence. The peak of the transgression is also concomitant with maxima in the clay and major elements. Depletion in oxygen levels at the sediment/water interface during the peak of the transgression is demonstrated by microfacies with increased lamination and poor fossil content, pristane/phytane ratios below one, and relatively low values of Mn/Al. Gammacerane content suggests prevailing water column stratification conducive to oxygen deficiency. However, re-oxygenation of the sediment-water interface led to either none or slight enrichment in the redox sensitive trace elements, mostly associated with sulfide phases.

A gradual reduction in the terrigenous supply began in the upper part of subunit 2b, where high-energy shoals with dominance of orbitolinids developed. This interval corresponds to the upper part of OAE-1a ($\delta^{13}\text{C}$ C6 stage), and the highstand system tract (HST) of the section. The highstand system tract, which started at the close of $\delta^{13}\text{C}$ C5 stage thus comprises the upper part of subunit 2b and continues into subunit 2c, coeval with the $\delta^{13}\text{C}$ C7 stage.

Lagoonal and rudist-dominated inner platform environments further developed in the early phase of $\delta^{13}\text{C}$ stage C7 subsequent to OAE-1a. The HST thus documents the slow change to carbonate sedimentation in oligotrophic conditions, as indicated by photozoan assemblages and drastic reduction of clay contents.

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7 SUMMARY AND CONCLUSIONS

The major objective of this work was to further understanding of the main forcing factors controlling the response of shallow-water environments to the worldwide Lower Aptian Oceanic Anoxic Event (OAE-1a), associated with major development of organic-carbon-rich levels. In order to accomplish this objective, two well-exposed sections were chosen from each other side of the Tethys: the Madotz section, Basco-Cantabrian Region of Spain, and the Curití section, Eastern Cordillera Tablazo-Magdalena Basin of Colombia. The study produced the following results:

A) I further assessed and updated the biochronology and correlation of organic-rich levels at Madotz and Curití relative to global Aptian anoxic events:

- The biochronology of the 62.5 m section at Madotz was revised using ammonite biostratigraphy, based on new specimens. New biostratigraphic data based on ammonites led to reinterpreting the timing of the different units of the Madotz section relative to OAE-1a. New taxa include *Deshayesites* cf. *forbesi* Casey, and *Pseudohaploceras*? sp. in the uppermost part of Unit 1, as well as *Deshayesites* cf. *forbesi* Casey, *Pseudosaynella bicurvata* (Michelin), and *Pseudosaynella raresulcata* (d'Orbigny) in the middle part of subunit 2b. These taxa support a stratigraphic position correlative with at least the upper part of the *Deshayesites forbesi* Zone, thus a lower stratigraphic position in the Lower Aptian (Bedoulian) than previously assigned to the section (e.g. Duvernois et al., 1972; Cherchi & Schroeder, 1998).
- At Curití, the Paja Formation overlies carbonate ramp deposits of the Rosablanca Fm with a top pyritic and phosphatic limestone containing phosphatized assemblages of middle Barremian to lowest Aptian ammonites of the genera *Pulchellia*, *Gerhardtia*, *Toxancycloceras*, *Karsteniceras* and *Prodeshayesites*. A lower Aptian position for the basal segment of the Paja Fm is confirmed as samples collected between 1.75 and 13.75

m above the base of the section contain calcareous nannofossil assemblages of the NC6 nannofossil zone. The base of the middle Aptian based on ammonite *Stoyanowiceras treffryanus* – *Dufrenoyia sanctorum* Zone (Etayo-Serna, 1979) is placed at 16.9 m from the base of the profile, slightly above the base of the NC7a nannofossil Zone (16.1m from the base of the profile).

B) I provided a detailed temporal paleoenvironmental reconstruction for the two sites based on a multiproxy approach using microfacies, mineralogy (XRD bulk and clays), elemental analyses (major, minor, trace elements, TIC), and organic geochemistry (Rock-Eval pyrolysis on bulk organic matter, total organic carbon and biomarker content, stable carbon isotopes on organic matter). These data provide valuable information that will enable future explorations in these areas to better evaluate their hydrocarbon potentials.

a) Madotz Section (Basco-Cantabrian Region)

- The interval studied includes siliciclastic Unit 1 (3 m) overlain in ascending order by subunits 2a (20 m), 2b (24.4 m) and 2c (basal 15 m studied) of the “Madotz Limestone”. Subunits 2a and 2c consist of Urgonian facies of pure carbonate deposits. In contrast, subunit 2b consists of carbonate-siliciclastic-mix facies (24.4 m-thick).
- The transition between Unit 1 and subunit 2a shows the progression from fossiliferous claystones (microfacies M1), litiolid foraminifera and bivalve rich biocalcarenes (microfacies M2), to packed and highly diverse calcirudites with corals, calcareous algae and minor rudistid bivalves (microfacies M3). The change from terrigenous sedimentation (Unit 1) to pure carbonates (subunit 2a) is indicative of shallowing, so microfacies M1 is interpreted as deposited below the fair-weather base, whereas microfacies M3 is interpreted as relatively high-energy deposits related to shoals in oligotrophic conditions.

- The lower part of Subunit 2b is characterized by abundant muddy orbitolinid-rich biocalcirudites and marlstones (microfacies M5), and interbeds of biopelmicrites (microfacies M6) and mudrocks with poor/absent orbitolinids (microfacies M6, M7, M8), some of which show low bioturbation index, poor in fossil content (few ostracods and calcispheres, rare/absent benthic foraminifers), pyrite and are relatively enriched in OM (microfacies M8). Sediments in subunit 2b accumulated in an outer platform/ramp to proximal platform slope setting, between the fair-weather wave base and above the storm wave base. Orbitolinid-dominated facies (M5) developed in slightly shallower environments than orbitolinid-poor/absent facies (M6, M7, and M8). Some of these levels are interpreted to experience periodic suboxic conditions (microfacies M7, M8). The upper part of subunit 2b is dominated by rounded orbitolinid biocalcirudites (microfacies M4) interpreted as an accumulation in high-energy regime, in shoals on the border of the platform.
- The base of subunit 2c characterized by miliolid and lituolid foraminiferal-rich biopelmicrites (Microfacies M9), is interpreted as lagoonal deposits transitioning into biopelmicrudites with diverse calcareous benthic faunas, including requieniid rudists (Microfacies M10) deposited in an internal carbonate platform.
- High-resolution stable carbon isotope results on bulk organic matter($\delta^{13}\text{C}_{\text{org}}$) carried out in Subunit 2b (26.6-49.2 m) show two excursions of 4.21‰ and 3.34‰, separated by a central segment with more uniform values around -22.56‰. Compared to the high-resolution $\delta^{13}\text{C}$ stratigraphy of the early Aptian of the Alpine Tethys (Menegatti et al., 1998), these two positive excursions correlate with segments C4 and C6 of OAE-1a, whereas the central segment is correlative with segment C5. Thus, the results indicate that the whole vertical extent of subunit 2b (24.4 m) is the local stratigraphic equivalent of OAE-1a, in agreement with other locations of the Iberian Peninsula.

- Rock-Eval pyrolysis on selected samples, as well as biomarkers indicate maturity levels in the Madotz section are within the oil window for the rock interval corresponding to OAE-1a.
- Calculated bulk sediment accumulation rates (without compaction correction) for the record of OAE-1a (C-isotope stages C4 and C6) at the study location range from 1.8 to 2.09 cm/kyr.
- Most of the clay-rich levels (M5, M6) deposited in fully or intermittently oxygenated water column (M7), in which reducing conditions and pyrite formation was mostly restricted to the porewaters, and did not lead to significant enrichment in organic matter or the redox sensitive trace elements.
- The 1.8 m-thick most prominent claystone and clay-shale beds (36–37.8m) in Subunit 2b with even lamination, rare fossils (microfacies M8; highest TOC: 0.4-0.97%), coincide with the peak of the transgression at that time. The geochemical proxies further indicate development of episodic hypoxic conditions. These beds contain pristane/phytane ratios reaching values of 0.88, and relatively low values of Mn/Al. Additionally, gammacerane content suggest water-column stratification. Hypoxic conditions are calculated to have lasted about 95.23 to 120 ky. Biomarker analyses suggest both marine and continental origin for the organic matter.
- Facies indicative of the existence of short episodes of oxygen deficiency at Madotz are restricted to the lower part of subunit 2b, correlating with C-isotope stage C4 and part of C5 synchronous with OAE-1a. Thus, at Madotz the temporal extent of relatively OM-rich facies indicative of oxygen depletion during OAE-1a is shorter than reported elsewhere in the literature for organic-rich shale facies in pelagic and hemipelagic environments. This finding demonstrates the effects of local physiographic factors in the response of the sedimentary basin to the overall global forcing factors associated with OAE-1a.

- Abrupt lithologic changes from the bioturbated claystones of Unit 1 to pure carbonate shoal facies of subunit 2a, are interpreted as the result of local reduction of terrigenous inputs, coeval with carbon isotope stage C2 (prior to OAE-1a), but a relative increase in smectite suggests a climatic change toward dried conditions. The lithologic change also involves a minor sequence boundary at the lowest part of Subunit 2a.
- Consistently high contents in major elements (Al, K, Ti, Si, Mg) and kaolinite/smectite ratios in shale samples from the lower part (14.7 m) of subunit 2b, correlative with ($\delta^{13}\text{C}_{\text{org}}$ segments C4-C5, are interpreted to indicate more humid climatic conditions during that interval of OAE-1a. The results provide evidence for sea level rise, episodic development of water column dysoxia, increased inputs of siliciclastics, terrestrial organic matter, and nutrients. The lower part of subunit 2b is interpreted as the transgressive system tract (TST) and the early (HST) of a Lower Aptian third-order sequence.

b) Curití Quarry Section (Eastern Cordillera of Colombia)

- The 1.56m interval of the Rosablanca Fm studied at Curití shows middle to outer carbonate ramp deposits that evolved rapidly from packed biocalcirudites to calcimudstones, and gradual increase in organic matter and phosphatic components. *Pulchellia* and *Pseudohaploceras* ammonite specimens indicate an upper Lower Barremian position for the top of the unit, or the *Pulchellia galeata* Zone (biozonation of Patarroyo, 2004)
- The basal 6.3m of Paja Fm are dominated by organic-rich marlstones, calcareous clay-shales and clay-shales lacking benthic fossils and bioturbation, and contain high organic matter. Such interval, particularly between 4.45 and 5.17cm (TOC, 2.99-8.84%; TIC, 19-70%) accumulated under prevalent oxygen-deficient conditions. The range of values and the overall pattern of the $\delta^{13}\text{C}_{\text{org}}$ curve (-22.05‰ and -20.47‰) within this 6.3-m interval,

of the Paja Fm is comparable with the Lower Aptian stable carbon isotope stage C7, which demonstrates for the first time by means of chemostratigraphy that the level rich in organic matter at Curití is subsequent to Oceanic Anoxic Event-1a, which is known to occur between stable carbon isotope stages C3 and C6.

- $T_{\max}$ temperature data from the Rock-Eval pyrolyses suggest that kerogen is within the end of oil window.
- The phosphatic bed at the top of the Rosablanca Fm (bed Co-09-6b) with phosphatized assemblages of middle Barremian, Upper Barremian and Lower Aptian ammonites is interpreted as a complex condensed/reworked bed. This bed encloses the time interval of OAE-1a, and most of the isotopic segments C3, C4, C5 and C6 of OAE-1a are apparently missing in this section.

APPENDICES

Appendix 1: Curití Quarry Calcareous Nannofossils, by Mihaela Melinte-Dobrinescu

General Characterization of the Encountered Nannofloras

The studied samples yielded a moderate to poor preservation (between 50 and 75 % could not be identified at species level). All the samples contain very high percentages of *Watznaueria barnesiae*, from 40-50 % up to 90 %. According to Roth and Krumbach (1986), assemblages that contain more than 40 % of *Watznaueria barnesiae* are heavily altered. This fact, together with the poor preservation and generally low diversity (number of the encountered taxa) and abundance (number of total specimens), indicate that the original composition of the assemblages was not preserved.

The identified calcareous nannofossil assemblages were assigned to the NC zones of Roth (1978). The nannofossil *Hayesites* (= *Rucinolithus*) *irregularis*, present from the base of the studied successions, is known to approximate the Barremian/Aptian boundary. It occurs slightly below the boundary, in the latest Barremian (Erba, 1996, Bersezio et al., 2002, Barrágan and Melinte, 2006, among others). Some authors (Bralower et al., 1997) indicate that the FO (first occurrence) of *Hayesites* (= *Rucinolithus*) *irregularis*, is placed at 121.0, therefore being coincident with the Barremian/Aptian boundary. The youngest event observed in the studied samples is the FO of *Eprolithus floralis* (placed at 119.0, according to Bralower et al., 1997).

Results

CO-11-73

Eprolithus floralis, *Rhagodiscus angustus*, *Biscutum* sp., *Braarudosphaera bigelowii*, *Chiastozygus litterarius*, *Cretarhabdus conicus*, *Flabellites oblongus*, *Lithraphidites carniolensis*, *Micrantholithus hoschulzii*, *M. obtusus*, *Nannoconus steinmannii*, *N. kamptneri*, *N. circularis*, *Repagulum parvidentatum*, *Rhagodiscus asper*, *Tegumentum stradneri*, *Zeugrhabdotus embergeri*, *Watznaueria barnesiae* (around 50 % of total nannofloras), *W. ovata*, *W. britannica*.

Age: Aptian (Nannofossil Zone NC7a)

Preservation: moderate

CO-11-59

Eprolithus floralis, *Rhagodiscus angustus*, *Chiastozygus litterarius*, *Cretarhabdus conicus*, *Cyclagelosphaera margerelii*, *Flabellites oblongus*, *Lithraphidites carniolensis*, *Micrantholithus hoschulzii*, *M. obtusus*, *Nannoconus steinmannii*, *N. kamptneri*, *N. circularis*, *Rhagodiscus asper*, *R. angustus*, *Tegumentum stradneri*, *Zeugrhabdotus embergeri*, *Z. erectus*, *Watznaueria barnesiae* (around 55 % of total nannofloras), *W. ovata*, *W. britannica*.

Age: Aptian (Nannofossil Zone NC7a)

Preservation: moderate

CO-11-57

Nannoconus cf. kamptneri, *Micrantholithus sp.*, *Zeugrhabdotus embergeri*, *Watznaueria barnesiae* (80 %), *W. ovata*.

Age: Early Cretaceous – all the taxa have a wide range; *Nannoconus kamptneri* and *Micrantholithus obtusus* have their last occurrence within the Aptian.

Preservation: poor.

CO-11-49

Hayesites irregularis, *Braarudosphaera hockwoldensis*, *Braarudosphaera batiliformis*, *Chiastozygus litterarius*, *Conusphaera mexicana*, *Eiffellithus cf. windii*, *Flabellites oblongus*, *Hayesites irregularis*, *Lithraphidites carniolensis*, *Micrantholithus obtusus*, *Nannoconus steinmannii*, *N. kamptneri*, *N. circularis*, *Rhagodiscus asper*, *Tegumentum stradneri*, *Zeugrhabdotus embergeri*, *Vagalapilla matalosa*, *Watznaueria barnesiae* (around 55 % of total nannofloras), *W. ovata*, *W. britannica*.

Age: NC6 nannofossil zone (NC6B subzone).

Preservation: moderate

CO-11-41a

Hayesites irregularis, *Braarudosphaera hockwoldensis*, *Braarudosphaera batiliformis*, *Chiastozygus litterarius*, *Conusphaera mexicana*, *Eiffellithus cf. windii*, *Flabellites oblongus*, *Hayesites irregularis*, *Lithraphidites carniolensis*, *Micrantholithus obtusus*, *Nannoconus steinmannii*, *N. kamptneri*, *N. circularis*, *Rhagodiscus asper*, *Tegumentum stradneri*, *Zeugrhabdotus embergeri*, *Vagalapilla matalosa*, *Watznaueria barnesiae* (around 55 % of total nannofloras), *W. ovata*, *W. britannica*.

Age: NC6 nannofossil zone (NC6B subzone).

Preservation: moderate

CO-11-33

Nannoconus steinmannii, *Micrantholithus obtusus*, *Zeugrhabdotus embergeri*, *Watznaueria barnesiae* (80 %), *W. ovata*.

Age: Early Cretaceous – all the taxa have a wide range; *Nannoconus steinmannii*, *Micrantholithus obtusus* have their last occurrence within the Aptian.

Preservation: poor.

CO-11-30

Nannoconus sp., *Zeugrhabdotus embergeri*, *Watznaueria barnesiae* (90 %), *W. ovata*.

Age: Cretaceous.

Preservation: poor.

CO-09-17c

Braarudosphaera hockwoldensis, *B. batiliformis*, *Hayesites irregularis*, *Braarudosphaera batiliformis* (known range Barremian/Aptian boundary interval), *Chiastozygus litterarius*, *Conusphaera mexicana*, *C. rothii*, *Flabellites oblongus*, *Hayesites irregularis*, *Lithraphidites carniolensis*, *Micrantholithus obtusus*, *Nannoconus steinmannii*, *N. kamptneri*, *N. circularis*,

Rhagodiscus asper, *Tegumentum stradneri*, *Zeugrhabdotus embergeri*, *Z. erectus*, *Vagalapilla matalosa*, *Watznaueria barnesiae* (around 45 % of total nannofloras), *W. ovata*, *W. britannica*.

Age: NC6 nannofossil zone (NC6A subzone). To note the presence of *Braarudosphaera hockwoldensis* with the known FO in the earliest Aptian.

Preservation: moderate (around 40 % of taxa are destroyed).

CO-09-9A

Hayesites irregularis, *Braarudosphaera batiliformis* (known range Barremian/Aptian boundary interval), *Chiastozygus* sp., *Conusphaera mexicana*, *C. rothii*, *Flabellites oblongus*, *Lithraphidites carniolensis*, *Manivitella pemmatoidea*, *Micrantholithus hoschulzii*, *M. obtusus*, *Nannoconus steinmannii*, *N. kamptneri*, *Rhagodiscus asper*, *Tegumentum stradneri*, *Zeugrhabdotus embergeri*, *Watznaueria barnesiae* (around 45 % of total nannofloras), *W. ovata*, *W. britannica*.

Age: NC6 nannofossil zone (NC6A subzone)

Preservation: moderate to poor (around 60 % of taxa are destroyed).

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Supplementary Table 1, Petrography of Madotz Section.

Abundance: rare (R), common (C), abundant (A), very abundant (VA). Fabric: alignment of clay minerals (ac), alignment of bioclasts (ab), alignment of organic matter fragments (aom), scour surfaces (sc), grain grading (grb), laminae showing variation in the abundance of carbonate grains (cvl), laminae showing variation in the abundance of quartz silt (svl). Primary fabric: matrix (MS), supported, grain- supported (CS). Particle orientation and internal structures: neomorphism of matrix or bioclasts (neo); micrite envelopes (micenv); dolomitization (dol); glauconite (glau); foram chamber infill (for); calcisphere, ostracod or mollusk chamber infill (foss); micritization taking place in bioclasts' walls (micbio); framboid and euhedral pyrite associated to agglutinated forams' walls or micrite envelopes (pywall); disseminated pyrite framboids (difr); phosphatized grains (phos). Roundness, primary fabric and abundance based on Flügel (2004) and references therein.

Supplementary Table 1, Petrography of Madotz Section.

Stratigraphic Unit	Distance from the base	Sample	Abundance of allochems (total count on 5 random fields)	Total Benthic forams	<i>P. lenticularis</i> , elongate:conic	Orbitolinids	%Orbitolinids	<i>Choffatella</i>	<i>Pseudocyclammina</i>	<i>Choffatella</i> + <i>Pseudocyclammina</i>	% <i>Choffatella</i> + <i>Pseudocyclammina</i>	<i>Lenticulina</i> sp.	% <i>Lenticulina</i>
	0	ES 06-03	R			0	0		0	0	0	0	0
1	3	ES 06-01	R			0	0		0	0	0	0	0
2a	3.2	ES 06-04	VA	61		0	0	16	11	27	9.71	0	0
2a	4.1	ES 06-02		0		0	0		0	0	0	0	0
2a	5	ES 06-05	VA	28	3:1-1:3	3	2.73	2	4	6	5.45	0	0
2a	6.12	ES 06-06	VA	0		0	0		0	0	0	0	0
2a	6.89	ES 06-07	VA	2		0	0	1	0	1	1.64	0	0
2a	8.59	ES 06-08	A	0		0	0		0	0	0	0	0
2a	9.35	ES 06-09	VA	1		1	2.17		0	0	0	0	0
2a	10.7	ES 06-10	VA	0		0	0		0	0	0	0	0
2a	12.5	ES 06-11	VA	0		0	0		0	0	0	0	0
2a	14.1	ES 06-12	VA	0		0	0		0	0	0	0	0
2a	15.7	ES 06-13	VA	0		0	0		0	0	0	0	0
2a	17.4	ES 06-14	VA	7	<1:3	4	4.12	1	0	1	1.03	0	0
2a	19.2	ES 06-15	VA	0		0	0		0	0	0	0	0
2a	20.7	ES 06-16	VA	1		0	0	1	0	1	1.43	0	0
2a	23	ES 06-17	VA	1		0	0		0	0	0	0	0
2b	26.6	ES-08-18a	A	4	>3:1	2	13.3		0	0	0	1	6.67
2b	26.9	ES-08-18b	VA	39	>3:1	26	18.2	8	0	8	5.59	1	0.7
2b	26.9	ES-08-18bb	VA	53	>3:1	41	29.7	6	0	6	4.35	3	2.17
2b	27.1	ES-08-18c nod	VA	7	>3:1	3	7.32		1	1	2.44	2	4.88
2b	27.4	ES-08-19	VA	14	>3:1	12	30	1	0	1	2.5	1	2.5
2b	27.6	ES-08-19a	A	8	>3:1	6	30		0	0	0	1	5
2b	27.8	ES-08-19b	C	1	>3:1	1	20		0	0	0	0	0
2b	27.9	ES-08-19d	VA	10	3:1	8	33.3		2	2	8.33	0	0
2b	28.1	ES-08-19c	C	3	>3:1	2	20		1	1	10	0	0
2b	28.8	ES-08-20	A	1		0	0		1	1	7.14	0	0
2b	29.1	ES-08-20b	VA	44	>3:1	33	31.4	4	0	4	3.81	1	0.95
2b	29.2	ES 06-21	A	6	>3:1	6	37.5		0	0	0	0	0
2b	29.5	ES 06-22	C	2		0	0		2	2	33.3	0	0
2b	29.9	ES 06-23	C	1		0	0		1	1	12.5	0	0
2b	30.1	ES 06-24	A	1		0	0		1	1	9.09	0	0
2b	30.5	ES 06-26	C	0		0	0		0	0	0	0	0
2b	30.7	ES 06-25	A	1		0	0		0	0	0	1	7.14
2b	31.4	ES 06-27	VA	32	>3:1	25	26.6	1	0	1	1.06	1	1.06
2b	32.1	ES 06-28	C	2		0	0		2	2	22.2	0	0
2b	32.5	ES 06-29	VA	6		0	0	1	1	2	6.9	1	3.45
2b	32.8	ES 06-30	C	1		0	0		0	0	0	0	0
2b	33	ES 06-31	VA	12		1	2.27	4	2	6	13.6	1	2.27

Supplementary Table 1, Continued...

Stratigraphic Unit	Distance from the base	Sample	Abundance of allochems (total count on 5 random fields)	Total Benthic forams	<i>P. lenticularis</i> , elongate:conic	Orbitolinids	%Orbitolinids	<i>Choffatella</i>	<i>Pseudocyclammina</i>	<i>Choffatella</i> + <i>Pseudocyclammina</i>	% <i>Choffatella</i> + <i>Pseudocyclammina</i>	<i>Lenticulina</i> sp.	% <i>Lenticulina</i>
2b	33.2	ES 06-32	VA	13		0	0	6	1	7	21.2	1	3.03
2b	33.3	ES 06-33	VA	6		0	0	1	0	1	4.55	0	0
2b	33.4	ES 06-34	C	1		0	0	1	0	1	16.7	0	0
2b	33.6	ES 06-35	C	0		0	0		0	0	0	0	0
2b	33.9	ES 06-36	F	0		0	0		0	0	0	0	0
2b	34.3	ES 06-37	F	0		0	0		0	0	0	0	0
2b	34.9	ES 06-38	A	5	>3:1	2	13.3	1	0	1	6.67	1	6.67
2b	34.9	ES 06-39	VA	8	>3:1	5	18.5	3	0	3	11.1	0	0
2b	35.3	ES 06-40	VA	37	>3:1	23	27.1	12	0	12	14.1	0	0
2b	35.6	ES 06-41	C	2		1	16.7	1	0	1	16.7	0	0
2b	35.9	ES 06-42	VA	8		1	2.56	3	3	6	15.4	0	0
2b	36.1	ES 06-43	C	0		0	0		0	0	0	0	0
		ES 06-44											
2b	36.4	(laminae)	VA	3		0	0	2	1	3	9.38	0	0
2b	36.4	ES 06-44	VA	1		0	0		1	1	4.17	0	0
2b	36.7	ES 06-45	VA	1		0	0		0	0	0	1	4.55
2b	36.9	ES 06-46	VA	0		0	0		0	0	0	0	0
2b	37.1	ES 06-47	A	1		0	0		1	1	5.56	0	0
2b	37.4	ES 06-48	C	0		0	0		0	0	0	0	0
2b	37.7	ES 06-49	C	0		0	0		0	0	0	0	0
2b	38.1	ES 06-50	C	1		0	0		0	0	0	0	0
2b	39.3	ES 06-51	VA	22	>3:1	10	17.2	12	0	12	20.7	0	0
2b	40.9	ES 06-52	A	7		6	27.3		1	1	4.55	0	0
2b	41.9	ES 06-53	VA	36	>3:1	33	38.4	1	0	1	1.16	0	0
2b	43.7	ES 08-54	VA	23	3:1-1:3	8	16	1	1	2	4	1	2
2b	44.2	ES 08-55	VA	40	>3:1	28	28.3	4	0	4	4.04	1	1.01
2b	44.7	ES 08-56	VA	51	3:1-1:3	29	24.8	8	0	8	6.84	1	0.85
2b	45.3	ES 08-57	VA	39	>3:1	31	29	4	2	6	5.61	0	0
2b	46.5	ES 08-58	VA	75	3:1-1:3	60	32.1	7	1	8	4.28	0	0
2c	48	ES-08-59	VA	56	>3:1	18	10.5	15	8	23	13.4	0	0
2c	49.5	ES-08-60	VA	84	3:1-1:3	7	3.4	14	5	19	9.22	0	0
2c	50	ES-08-61	VA	62	>3:1	11	6.43	24	3	27	15.8	1	0.58
2c	50.1	ES-08-61A	VA	58	>3:1	1	0.6	8	1	9	5.36	0	0
2c	52.5	ES-08-62	VA	47		5	3.18	19	6	25	15.9	0	0
2c	53.8	ES-08-63	VA	50		0	0	25	14	39	20.7	1	0.53
2c	58.5	ES-08-64	VA	23		0	0		0	0	0	0	0
2c	60.8	ES-08-65	C	1		0	0		0	0	0	0	0

Supplementary Table 1, Continued...

Sample	Miliolids	%Miliolids	Ostracods	%Ostracods	Calcisphaerae	%Calcisphaerae	Udoteacean (<i>Boueina</i> sp.)	%Udoteacean (<i>Boueina</i> sp.)	Gymnocodiantacean and Dacyclad	Corallinacean Red Algae	Bivalves (non-rudist)	%Bivalves (non-rudist)	Rudist	%Rudist	Gastropods
ES 06-03	0	0	0	0	0	0	0	0	0	0	1	100	0	0	0
ES 06-01	0	0	0	0	0	0	0	0	0	0	1	100	0	0	0
ES 06-04	1	0.36	0	0	2	0.7	0	0	1	0	160	58	0	0	10
ES 06-02	0	0	0	0	0	0	0	0	0	0	3	30	0	0	0
ES 06-05	0	0	0	0	0	0	0	0	0	0	68	62	0	0	0
ES 06-06	0	0	0	0	0	0	3	6.38	0	0	11	23	0	0	3
ES 06-07	0	0	0	0	0	0	3	4.92	0	0	18	30	0	0	0
ES 06-08	0	0	0	0	0	0	0	0	0	0	4	67	0	0	0
ES 06-09	0	0	0	0	0	0	2	4.35	0	0	5	11	0	0	0
ES 06-10	0	0	0	0	0	0	3	3.33	0	0	24	27	0	0	0
ES 06-11	0	0	0	0	0	0	16	22.5	0	0	19	27	0	0	0
ES 06-12	0	0	0	0	0	0	4	6.06	0	0	40	61	0	0	0
ES 06-13	0	0	0	0	0	0	6	10.3	0	0	26	45	0	0	0
ES 06-14	1	1.03	0	0	0	0	9	9.28	1	1	58	60	0	0	1
ES 06-15	0	0	0	0	0	0	9	13.8	3	0	24	37	3	4.6	0
ES 06-16	0	0	0	0	0	0	2	2.86	0	0	21	30	1	1.4	0
ES 06-17	0	0	0	0	0	0	23	30.7	1	0	28	37	0	0	0
ES-08-18a	0	0	0	0	0	0	0	0	0	0	6	40	0	0	0
ES-08-18b	0	0	0	0	0	0	0	0	0	0	20	14	0	0	0
ES-08-18bb	0	0	0	0	1	0.7	0	0	0	0	26	19	0	0	0
ES-08-18c nod	0	0	0	0	1	2.4	0	0	0	0	12	29	0	0	0
ES-08-19	0	0	0	0	1	2.5	0	0	0	0	8	20	0	0	0
ES-08-19a	0	0	0	0	0	0	0	0	0	0	3	15	0	0	0
ES-08-19b	0	0	0	0	2	40	0	0	0	0		0	0	0	0
ES-08-19d	0	0	0	0	2	8.3	0	0	0	0	2	8.3	0	0	0
ES-08-19c	0	0	0	0	2	20	0	0	0	0	2	20	0	0	0
ES-08-20	0	0	1	7.1	6	43	0	0	0	0	3	21	0	0	0
ES-08-20b	2	1.9	0	0	1	1	0	0	0	0	13	12	0	0	0
ES 06-21	0	0	0	0	0	0	0	0	0	0	1	6.3	0	0	0
ES 06-22	0	0	0	0	1	17	0	0	0	0		0	0	0	0
ES 06-23	0	0	0	0	2	25	0	0	0	0		0	0	0	0
ES 06-24	0	0	0	0	2	18	0	0	0	0	1	9.1	0	0	0
ES 06-26	0	0	0	0	0	0	0	0	0	0	7	70	0	0	0
ES 06-25	0	0	0	0	1	7.1	0	0	0	0	7	50	0	0	0
ES 06-27	0	0	0	0	5	5.3	0	0	0	0	14	15	0	0	0
ES 06-28	0	0	0	0	1	11	0	0	0	0	4	44	0	0	0
ES 06-29	2	6.9	0	0	1	3.4	0	0	0	0	6	21	0	0	0
ES 06-30	0	0	0	0	0	0	0	0	0	0	3	50	0	0	0
ES 06-31	0	0	0	0	2	4.5	0	0	0	0	9	20	0	0	0

Supplementary Table 1, Continued...

Sample	Miliolids	%Miliolids	Ostracods	%Ostracods	Calcisphaerae	%Calcisphaerae	Udoteacean (<i>Boueina</i> sp.)	%Udoteacean (<i>Boueina</i> sp.)	Gymnocodiantacean and Dacyclad	Corallinacean Red Algae	Bivalves (non-rudist)	%Bivalves (non-rudist)	Rudist	%Rudist	Gastropods
ES 06-32	0	0	0	0	1	3	0	0	0	0	4	12	0	0	0
ES 06-33	0	0	0	0	1	4.5	0	0	0	0	5	23	0	0	0
ES 06-34	0	0	0	0	1	17	0	0	0	0		0	0	0	0
ES 06-35	0	0	0	0	0	0	0	0	0	0	1	33	0	0	0
ES 06-36	0	0	0	0	0	0	0	0	0	0	2	100	0	0	0
ES 06-37	0	0	1	50	1	50	0	0	0	0		0	0	0	0
ES 06-38	0	0	1	6.7	1	6.7	0	0	0	0	3	20	0	0	0
ES 06-39	0	0	0	0	1	3.7	0	0	0	0	7	26	0	0	0
ES 06-40	0	0	0	0	2	2.4	0	0	0	0	1	1.2	0	0	0
ES 06-41	0	0	0	0	2	33	0	0	0	0		0	0	0	0
ES 06-42	0	0	0	0	2	5.1	0	0	0	0	17	44	0	0	0
ES 06-43	0	0	1	14	1	14	0	0	0	0	3	43	0	0	0
ES 06-44 (laminae)	0	0	3	9.4	3	9.4	0	0	0	0	11	34	0	0	1
ES 06-44	0	0	4	17	15	63	0	0	0	0	1	4.2	0	0	0
ES 06-45	0	0	5	23	13	59	0	0	0	0		0	0	0	0
ES 06-46	0	0	6	26	10	43	0	0	0	0	2	8.7	0	0	0
ES 06-47	0	0	1	5.6	4	22	0	0	0	0	9	50	0	0	0
ES 06-48	0	0	0	0	1	33	0	0	0	0	1	33	0	0	0
ES 06-49	0	0	0	0	6	67	0	0	0	0	0	0	0	0	0
ES 06-50	0	0	0	0	1	25	0	0	0	0	1	25	0	0	0
ES 06-51	0	0	0	0	0	0	0	0	0	0	2	3.4	0	0	0
ES 06-52	0	0	0	0	0	0	0	0	0	0	3	14	0	0	0
ES 06-53	0	0	0	0	0	0	0	0	0	0	5	5.8	0	0	0
ES 08-54	1	2	0	0	1	2	0	0	0	0	7	14	0	0	0
ES 08-55	0	0	0	0	0	0	0	0	0	0	10	10	1	1	1
ES 08-56	0	0	0	0	0	0	0	0	0	0	7	6	0	0	0
ES 08-57	0	0	0	0	0	0	0	0	0	0	16	15	1	0.9	1
ES 08-58	0	0	0	0	0	0	0	0	0	0	21	11	1	0.5	3
ES-08-59	1	0.58	0	0	0	0	0	0	0	0	58	34	1	0.6	0
ES-08-60	42	20.4	0	0	2	1	0	0	0	0	37	18	1	0.5	0
ES-08-61	12	7.02	0	0	5	2.9	0	0	0	0	33	19	0	0	0
ES-08-61A	43	25.6	0	0	0	0	0	0	0	0	40	24	0	0	1
ES-08-62	11	7.01	0	0	0	0	0	0	0	0	48	31	0	0	0
ES-08-63	6	3.19	0	0	2	1.1	1	0.53	0	0	49	26	3	1.6	0
ES-08-64	17	17	0	0	0	0	1	1	1	0	5	5	45	45	0
ES-08-65	0	0	0	0	0	0	0	0	0	0	2	8	20	80	0

Supplementary Table 1, Continued...

Sample	Corals	%Corals	Sponges	%Sponges	Bryozoans	%Bryozoans	Brachiopods	%Brachiopods	Echinoids	%Echinoids	Serpulids	Total Benthic forams	% Benthic forams	Total fossils
ES 06-03	0	0	0	0	0	0	0	0	0	0	0	0	0	1
ES 06-01	0	0	0	0	0	0	0	0	0	0	0	0	0	1
ES 06-04	0	0	0	0	0	0	0	0	16	5.8	0	61	21.9	278
ES 06-02	0	0	6	60	0	0	0	0	1	10	0	0	0	10
ES 06-05	1	0.9	0	0	0	0	0	0	4	3.6	0	28	25.5	110
ES 06-06	23	49	2	4.3	0	0	0	0	5	11	0	0	0	47
ES 06-07	20	33	8	13	0	0	0	0	9	15	0	2	3.28	61
ES 06-08	0	0	1	17	0	0	0	0	1	17	0	0	0	6
ES 06-09	22	48	5	11	4	9	0	0	5	11	1	1	2.17	46
ES 06-10	36	40	7	7.8	3	3	0	0	17	19	0	0	0	90
ES 06-11	17	24	4	5.6	3	4	0	0	12	17	0	0	0	71
ES 06-12	4	6.1	0	0	2	3	0	0	16	24	0	0	0	66
ES 06-13	4	6.9	2	3.4	2	3	0	0	18	31	0	0	0	58
ES 06-14	10	10	0	0	0	0	0	0	4	4.1	0	7	7.22	97
ES 06-15	11	17	1	1.5	0	0	0	0	14	22	0	0	0	65
ES 06-16	4	5.7	13	19	2	3	0	0	25	36	0	1	1.43	70
ES 06-17	0	0	8	11	3	4	0	0	11	15	0	1	1.33	75
ES-08-18a	0	0	0	0	0	0	0	0	2	13	0	4	26.7	15
ES-08-18b	0	0	0	0	0	0	3	2.1	46	32	0	39	27.3	143
ES-08-18bb	0	0	0	0	0	0	0	0	8	5.8	0	53	38.4	138
ES-08-18c nod	0	0	0	0	0	0	0	0	15	37	0	7	17.1	41
ES-08-19	0	0	0	0	0	0	0	0	3	7.5	0	14	35	40
ES-08-19a	0	0	0	0	0	0	1	5	1	5	0	8	40	20
ES-08-19b	0	0	0	0	0	0	1	20	0	0	0	1	20	5
ES-08-19d	0	0	0	0	0	0	0	0	0	0	0	10	41.7	24
ES-08-19c	0	0	0	0	0	0	0	0	0	0	0	3	30	10
ES-08-20	0	0	0	0	0	0	1	7.1	1	7.1	0	1	7.14	14
ES-08-20b	0	0	0	0	0	0	0	0	7	6.7	0	44	41.9	105
ES 06-21	0	0	0	0	0	0	0	0	3	19	0	6	37.5	16
ES 06-22	0	0	0	0	0	0	0	0	1	17	0	2	33.3	6
ES 06-23	0	0	0	0	0	0	0	0	4	50	0	1	12.5	8
ES 06-24	0	0	0	0	0	0	1	9.1	4	36	1	1	9.09	11
ES 06-26	0	0	0	0	0	0	0	0	3	30	0	0	0	10
ES 06-25	0	0	0	0	0	0	0	0	4	29	0	1	7.14	14
ES 06-27	0	0	0	0	0	0	0	0	15	16	1	32	34	94
ES 06-28	0	0	0	0	0	0	0	0	0	0	0	2	22.2	9
ES 06-29	0	0	0	0	0	0	0	0	11	38	0	6	20.7	29
ES 06-30	0	0	0	0	0	0	0	0	2	33	0	1	16.7	6
ES 06-31	0	0	0	0	0	0	0	0	13	30	0	12	27.3	44

Supplementary Table 1, Continued...

Sample	Corals	%Corals	Sponges	%Sponges	Bryozoans	%Bryozoans	Brachiopods	%Brachiopods	Echinoids	%Echinoids	Serpulids	Total Benthic forams	% Benthic forams	Total fossils
ES 06-32	0	0	0	0	0	0	0	0	7	21	0	13	39.4	33
ES 06-33	0	0	0	0	0	0	0	0	9	41	0	6	27.3	22
ES 06-34	0	0	0	0	0	0	0	0	3	50	0	1	16.7	6
ES 06-35	0	0	0	0	0	0	0	0	2	67	0	0	0	3
ES 06-36	0	0	0	0	0	0	0	0	0	0	0	0	0	2
ES 06-37	0	0	0	0	0	0	0	0		0	0	0	0	2
ES 06-38	0	0	0	0	0	0	0	0	1	6.7	0	5	33.3	15
ES 06-39	0	0	0	0	0	0	0	0	3	11	0	8	29.6	27
ES 06-40	0	0	0	0	0	0	1	1.2	8	9.4	1	37	43.5	85
ES 06-41	0	0	0	0	0	0	0	0	0	0	0	2	33.3	6
ES 06-42	0	0	0	0	0	0	0	0	5	13	0	8	20.5	39
ES 06-43	0	0	0	0	0	0	0	0	2	29	0	0	0	7
ES 06-44														
(laminae)	0	0	0	0	0	0	0	0	8	25	0	3	9.38	32
ES 06-44	0	0	0	0	0	0	0	0	2	8.3	0	1	4.17	24
ES 06-45	0	0	0	0	0	0	0	0	2	9.1	0	1	4.55	22
ES 06-46	0	0	0	0	0	0	0	0	5	22	0	0	0	23
ES 06-47	0	0	0	0	0	0	0	0	2	11	0	1	5.56	18
ES 06-48	0	0	0	0	0	0	0	0	1	33	0	0	0	3
ES 06-49	0	0	0	0	0	0	0	0	3	33	0	0	0	9
ES 06-50	0	0	0	0	0	0	0	0	1	25	0	1	25	4
ES 06-51	0	0	0	0	0	0	0	0	12	21	0	22	37.9	58
ES 06-52	0	0	0	0	0	0	0	0	5	23	0	7	31.8	22
ES 06-53	0	0	0	0	0	0	0	0	11	13	0	36	41.9	86
ES 08-54	0	0	0	0	0	0	0	0	7	14	0	23	46	50
ES 08-55	0	0	0	0	0	0	2	2	12	12	0	40	40.4	99
ES 08-56	0	0	0	0	0	0	0	0	21	18	0	51	43.6	117
ES 08-57	0	0	0	0	0	0	0	0	13	12	0	39	36.4	107
ES 08-58	0	0	0	0	1	1	0	0	18	9.6	0	75	40.1	187
ES-08-59	0	0	0	0	0	0	1	0.6	11	6.4	3	56	32.6	172
ES-08-60	0	0	0	0	0	0	2	1	12	5.8	0	84	40.8	206
ES-08-61	1	0.6	0	0	0	0	1	0.6	18	11	0	62	36.3	171
ES-08-61A	0	0	0	0	0	0	1	0.6	15	8.9	0	58	34.5	168
ES-08-62	1	0.6	0	0	0	0	0	0	20	13	0	47	29.9	157
ES-08-63	15	8	0	0	1	1	1	0.5	20	11	0	50	26.6	188
ES-08-64	1	1	0	0	0	0	0	0	7	7	0	23	23	100
ES-08-65	1	4	0	0	0	0	0	0	1	4	0	1	4	25

Supplementary Table 1, Continued...

Sample	bioclasts : cortoids	Bioclasts+cortoids : peloids	Aggregate grains	Intraclasts	Size sorting (allochems)	Rounded : Angular bioclasts	Bioperturbation index	Lamination
ES 06-03	>>3:1	>>3:1	0	0			3	no
ES 06-01	>>3:1	>>3:1	0	0			3	no
ES 06-04	>3:1	>>3:1	0	0	Poor	<1:3	3	no
ES 06-02	>3:1	>>3:1	0	0	Poor?		3	no
ES 06-05	3:1-1:3	>3:1	5	0	Poorly/Very poorly	>3:1	3	no
ES 06-06	3:1-1:3	>>3:1	1	0	Poorly/Very poorly	>3:1	3	no
ES 06-07	3:1-1:3	>>3:1	4	0	Moderately/Poorly	>3:1	3	no
ES 06-08	>3:1	>>3:1	0	0	Poorly/Very poorly	>3:1	3	no
ES 06-09	3:1-1:3	>>3:1	1	0	Moderately well/Moderately	>3:1	3	no
ES 06-10	3:1-1:3	>>3:1	4	3	Moderately well/Moderately	>3:1	3	no
ES 06-11	<1:3	>>3:1	0	1	Moderately well/Moderately	>3:1	3	no
ES 06-12	>3:1	>>3:1	0	0	Poorly/Very poorly	>3:1	3	no
ES 06-13	>3:1	3:1-1:3	0	0	Poorly/Very poorly	>3:1	3	no
ES 06-14	3:1-1:3	>>3:1	9	0	Moderately well/Moderately	>3:1	3	no
ES 06-15	3:1-1:3	>>3:1	0	0	Poorly/Very poorly	>3:1	3	no
ES 06-16	3:1-1:3	>>3:1	1	0	Moderately/Poorly	>3:1	3	no
ES 06-17	3:1-1:3	>>3:1	0	0	Poorly/Very poorly	>3:1	1	no
ES-08-18a	3:1-1:3	>>3:1	0	0	Poorly/Very poorly	<1:3	3	no
ES-08-18b	<1:3	>>3:1	0	0	Moderately/Poorly	<1:3	1	no
ES-08-18bb	>>3:1	>>3:1	0	0	Well/Moderately well	<1:3	1	no
ES-08-18c nod	3:1-1:3	>>3:1	0	0	Poorly/Very poorly	<1:3	3	no
ES-08-19	>3:1	>>3:1	0	0	Well/Moderately well	<1:3	3	no
ES-08-19a	3:1-1:3	>>3:1	0	0	Poorly/Very poorly	<1:3	1	some?
ES-08-19b	>>3:1	>>3:1	0	0	Poorly/Very poorly	<<1:3	3	no
ES-08-19d	3:1-1:3	>>3:1	0	0	Poorly/Very poorly	<<1:3	1	no
ES-08-19c	>>3:1	>>3:1	0	0	Poorly/Very poorly	<<1:3	3	no
ES-08-20	>>3:1	>>3:1	0	0	Poorly/Very poorly	<<1:3	2	no
ES-08-20b	>3:1	>>3:1	0	0	Moderately well/Moderately	<<1:3	1	no
ES 06-21	>>3:1	>>3:1	0	0	Poorly/Very poorly	<<1:3	1	no
ES 06-22	>>3:1	>>3:1	0	0	Poorly/Very poorly	<<1:3	2	no
ES 06-23	>>3:1	<1:3	0	0	Poorly/Very poorly	<<1:3	1	some
ES 06-24	>>3:1	3:1-1:3	0	0	Poorly/Very poorly	<<1:3	2	some
ES 06-26	>>3:1	>>3:1	0	0	Poorly/Very poorly	<<1:3	1	some
ES 06-25	>>3:1	>>3:1	0	0	Poorly/Very poorly	<<1:3	1	some?
ES 06-27	>3:1	>3:1	0	0	Moderately/Poorly	<<1:3	1	no
ES 06-28	>>3:1	>>3:1	0	0	Poorly/Very poorly	<<1:3	2	some
ES 06-29	>>3:1	3:1-1:3	0	0	Poorly/Very poorly	<<1:3	3	no
ES 06-30	>>3:1	>>3:1	0	0	Poorly/Very poorly	<<1:3	1	some
ES 06-31	>3:1	3:1-1:3	0	0	Poorly/Very poorly	<<1:3	4	no

Supplementary Table 1, Continued...

Sample	bioclasts : cortoids	Bioclasts+cortoids : peloids	Aggregate grains	Intraclasts	Size sorting (allochems)	Rounded : Angular bioclasts	Bioperturbation index	Lamination
ES 06-32	>>3:1		0	0	Poorly/Very poorly	<<1-3	4	no
ES 06-33	>>3:1	3:1-1:3	0	0	Poorly/Very poorly	<<1-3	3	no
ES 06-34	>>3:1	3:1-1:3	0	0	Poorly/Very poorly	<<1-3	3	no
ES 06-35	>>3:1	<1:3	0	0	Poorly/Very poorly	<<1-3	4	no
ES 06-36	>>3:1	3:1-1:3	0	0	Poorly/Very poorly	<<1-3	4	no
ES 06-37	>>3:1	>>3:1	0	0	Poorly/Very poorly	<<1-3	3?	no
ES 06-38	>>3:1	>>3:1	0	0	Poorly/Very poorly	<<1-3	4	no
ES 06-39	>>3:1	>>3:1	0	0	Poorly/Very poorly	<<1-3	3	no
ES 06-40	3:1-1:3	3:1-1:3	0	0	Moderately/Poorly	<<1-3	2	no
ES 06-41	>>3:1	>>3:1	0	0	Poorly/Very poorly	<<1-3	3?	no
ES 06-42	>>3:1	3:1-1:3	0	0	Poorly/Very poorly	<<1-3	2	some
ES 06-43	>>3:1	>>3:1	0	0	Poorly/Very poorly	<<1-3	4	no
ES 06-44 (laminae)	>>3:1	>>3:1	0	0	Poorly/Very poorly	<<1-3	1	yes
ES 06-44	>>3:1	>>3:1	0	0	Poorly/Very poorly	<<1-3	1	yes
ES 06-45	>>3:1	>>3:1	0	0	Poorly/Very poorly	<<1-3	2	yes
ES 06-46	>>3:1	>>3:1	0	0	Poorly/Very poorly	<<1-3	1	yes
ES 06-47	>>3:1	>>3:1	0	0	Poorly/Very poorly	<<1-3	2	some
ES 06-48	>>3:1	>>3:1	0	0	Poorly/Very poorly	<<1-3	1	some
ES 06-49	>>3:1	>>3:1	0	0	Poorly/Very poorly	<<1-3	3	no
ES 06-50	>>3:1	>>3:1	0	0	Poorly/Very poorly	<<1-3	3	no
ES 06-51	>3:1	3:1-1:3	0	0	Poorly/Very poorly	<1:3	2	no
ES 06-52	3:1-1:3	3:1-1:3	0	0	Poorly/Very poorly	<1:3	2	no
ES 06-53	>3:1	>3:1	0	0	Very well/well	<1:3	1	no
ES 08-54	<1:3	>3:1	0	0	Poorly/Very poorly	>3:1	1	no
ES 08-55	<1:3	>3:1	0	0	Moderately/Poorly	>3:1	2	
ES 08-56	<1:3	3:1-1:3	0	0	Poorly/Very poorly	>3:1	1	no
ES 08-57	3:1-1:3	>3:1	0	0	Moderately/Poorly	<1:3	1	no
ES 08-58	3:1-1:3	>3:1	0	0	Moderately/Poorly	>3:1	1	no
ES-08-59	3:1-1:3	>3:1	0	0	Poorly/Very poorly	3:1-1:3	1	no
ES-08-60	>3:1	3:1-1:3	0	0	Poorly/Very poorly	<1:3	1	no
ES-08-61	>3:1	3:1-1:3	0	0	Poorly/Very poorly	<1:3	5	no
ES-08-61A	>3:1	3:1-1:3	0	0	Poorly/Very poorly	<1:3	1	no
ES-08-62	>3:1	3:1-1:3	0	2	Poorly/Very poorly	<1:3	2	no
ES-08-63	>3:1	>3:1	0	0	Poorly/Very poorly	3:1-1:3	1	no
ES-08-64	<1:3	<1:3	0	0	Poorly/Very poorly	3:1-1:3	5	no
ES-08-65	>3:1	>3:1	0	0	Poorly/Very poorly	<1:3	5	no

Supplementary Table 1, Continued...

Sample	Particle orientation and internal structures	Primary fabric (matrix-supported, grain-supported)	%Matrix (calcareous terrigenous)	Calcareous matrix vs. terrigenous clay matrix
ES 06-03	fair (ac)	MS	>95%	calcareous silt, pellets <<clay minerals
ES 06-01	fair (ac)	MS	>95%	calcareous silt, pellets<<clay minerals
ES 06-04	good (ab)	MS	70%	micrite
ES 06-02		?	<10%	micrite, microspar
ES 06-05	poor (ab)	MS-GS	40-50%	microspar
ES 06-06	absent	GS	40-50%	microspar
ES 06-07	poor (ab)	MS	60%	microspar
ES 06-08		?	20-30%	micrite
ES 06-09	absent	GS	30-40%	micrite, microspar
ES 06-10	absent	GS	40-50%	micrite
ES 06-11	poor (ab)	GS	40%	micrite
ES 06-12	Google	MS	60%	micrite
ES 06-13	absent	MS	60-70%	micrite
ES 06-14	absent	GS	40%	micrite, microspar
ES 06-15	absent	GS	40-50%	micrite
ES 06-16	absent	GS	50%	micrite, pseudospar
ES 06-17	absent	MS	50-60%	micrite
ES-08-18a	poor (cvl, ac)	MS	90%	calcareous silt>>clay minerals
ES-08-18b	fair (cvl, sc, ab)	GS, MS	75-50%	calcareous silt>clay minerals
ES-08-18bb	fair (cvl, ab)	GS, MS	50-60%	calcareous silt>clay minerals
ES-08-18c nod	poor	MS	>90%	calcareous silt>clay minerals
ES-08-19	poor	MS	70%	calcareous silt>clay minerals
ES-08-19a	fair (ac, ab)	MS	>90%	calcareous silt<<clay minerals
ES-08-19b	poor	MS	>95%	calcareous silt<<clay minerals
ES-08-19d	fair (ac, ab)	MS	>90%	calcareous silt<<clay minerals
ES-08-19c	poor (ac, ab)	MS	>95%	calcareous silt<<clay minerals
ES-08-20	absent (aom)	MS	>95%	micrite>clay minerals
ES-08-20b	fair (ac, ab)	MS	50-60%	calcareous silt<<clay minerals
ES 06-21	fair (ac, ab)	MS	>95%	calcareous silt<<clay minerals
ES 06-22	fair (ac, aom)	MS	>95%	calcareous silt<<clay minerals
ES 06-23	fair (ac, aom)	MS	>95%	calcareous silt+pellets<<clay minerals
ES 06-24	absent	MS	>95%	calcareous silt and micrite>clay minerals
ES 06-26	poor (ac, aom)	MS	>95%	calcareous silt<clay minerals
ES 06-25	poor (ac, aom)	MS	>95%	calcareous silt<clay minerals
ES 06-27	fair (ab)	GS,MS	60-80%	calcareous silt>clay minerals
ES 06-28	fair (ac, aom)	MS	>>99%	calcareous silt<<clay minerals
ES 06-29	poor (ab, aom)	MS	>95%	calcareous silt>clay minerals
ES 06-30	fair (ac, aom)	MS	>95%	calcareous silt<<clay minerals
ES 06-31	absent	MS	~70-80%	calcareous silt+micrite>clay minerals

Supplementary Table 1, Continued...

Sample	Particle orientation and internal structures	Primary fabric (matrix-supported, grain-supported)	+ %Matrix (calcareous terrigenous)	Calcareous matrix vs. terrigenous clay matrix
ES 06-32	absent	MS	>90%	calcareous silt<<clay minerals
ES 06-33	poor	MS	~80%	calcareous silt+pellets>clay minerals
ES 06-34	poor	MS	>95%	calcareous silt<<clay minerals
ES 06-35	absent	MS	>90%	calcareous silt+pellets=clay minerals
ES 06-36	absent	MS	>99%	calcareous mud<<clay minerals
ES 06-37	fair (ac, aom)	MS	>95%	calcareous silt<<clay minerals
ES 06-38	poor (ab)	MS	~99%	calcareous silt<<clay minerals
ES 06-39	absent	MS	>95%	calcareous silt<<clay minerals
ES 06-40	fair (ac, ab)	MS-GS	50-60%	calcareous silt<<clay minerals
ES 06-41	fair (ac, aom)	MS	>95%	calcareous silt+pellets<<clay minerals
ES 06-42	poor	MS	80-90%	calcareous silt+pellets>clay minerals
ES 06-43	poor	MS	>95%	calcareous silt+pellets<<clay minerals
S 06-44 (lamina)	good (svl, ab)	MS	>90%	(thin lamina)
ES 06-44	good (ac, aom, svl)	MS	>95%	calcareous silt+pellets<<clay minerals
ES 06-45	fair (ac, aom)	MS	>95%	calcareous silt+pellets<<clay minerals
ES 06-46	fair-good (ac, aom)	MS	>95%	calcareous silt+pellets<<clay minerals
ES 06-47	fair (ac, aom)	MS	>95%	calcareous silt+pellets<<clay minerals
ES 06-48	good (ac, aom)	MS	>95%	calcareous silt+pellets<<clay minerals
ES 06-49	poor (ac, aom)	MS	>95%	calcareous silt+pellets<<clay minerals
ES 06-50	poor (ac, aom, ab)	MS	>95%	calcareous silt<<clay minerals
ES 06-51	poor (ac, ab)	MS	80-90%	calcareous silt+pellets<clay minerals
ES 06-52	poor (ac, ab)	MS	>90%	calcareous silt<<clay minerals
ES 06-53	fair (ab)	GS	~50%	calcareous silt and micrite>clay minerals
ES 08-54	absent	GS	~50%	micrite
ES 08-55	fair (ab)	GS	50-60%	micrite>>clay minerals
ES 08-56	absent	GS	50-60%	micrite
ES 08-57	absent	GS-MS	80-60%	calcareous silt + micrite>clay minerals
ES 08-58	absent (ab)	GS	~60%	micrite
ES-08-59	absent	MS	~60%	micrite
ES-08-60	absent (ab)	MS	50-60%	micrite
ES-08-61	absent	MS	40%	calcareous silt + micrite
ES-08-61A	absent	MS	50%	calcareous silt + micrite
ES-08-62	absent (ab)	MS	40%	calcareous silt + micrite
ES-08-63	absent (ab)	MS	~60%	calcareous silt + micrite<clay minerals
ES-08-64	absent (ab)	GS	40%	micrite, microspar
ES-08-65	absent (ab)	MS	70-80%	micrite

Supplementary Table 1, Continued...

Sample	Quartz	Diagenetic Features	Pyrite
ES 06-03	~1% (silt)	difr	yes
ES 06-01	~1% (silt)	drfr	
ES 06-04	7.50%	neo, micenv, pywall	yes
ES 06-02	0%	neo	
ES 06-05	<1%	neo, micenv, for (glau)	
ES 06-06	0%	neo, micenv	
ES 06-07	0%	neo, micenv, for (py), pywall	yes
ES 06-08	0%	neo, micenv	
ES 06-09	0%	neo, micenv	
ES 06-10	0%	neo, micenv	
ES 06-11	0%	neo, micenv	
ES 06-12	0%	neo	
ES 06-13	0%	neo	
ES 06-14	0%	neo, micenv, micbio	
ES 06-15	0%	neo, micenv, micbio	
ES 06-16	0%	neo, micenv	
ES 06-17	0%	neo, micenv, dol, for (py), pywall	yes
ES-08-18a	5% (mainly silt)	micenv, pywall, difr	yes
ES-08-18b	1-5% (mainly silt)	neo, micbio, for(py), pywall, difr	yes
ES-08-18bb	5% (mainly silt)	neo, micbio, difr, for (py), pywall	yes
ES-08-18c nod	2.5% (silt, very fine sand)	micbio, difr	yes
ES-08-19	2.5% (mainly silt)	neo, micbio, for(py), difr	yes
ES-08-19a	2.5% (mainly silt)	micbio, difr, for (py)	yes
ES-08-19b	1% (mainly silt)	difr, for (py), from	yes
ES-08-19d	2.5% (mainly silt)	from, difr?	yes
ES-08-19c	1 % (mainly silt)		no
ES-08-20	2.5% (silt, very fine sand)	micbio, from?, foss (py)	yes
ES-08-20b	2.5% (silt)	neo, micbio	no
ES 06-21	2.5% (silt)	from?, for(py)	yes
ES 06-22	5% (silt)	from?, for(py)	yes
ES 06-23	2.5% (mostly silt)	difr	yes
ES 06-24	5% (silt)	difr, from?	yes
ES 06-26	7.5% (silt)	difr, from?	yes
ES 06-25	7.5% (silt)	nod, difr	yes
ES 06-27	5% (mainly silt)	neo, micbio	yes
ES 06-28	5% (mainly silt)	difr, foss (py), for (py), from	yes
ES 06-29	7.5% (silt)	neo, micenv, for (py), foss (py), from	yes
ES 06-30	5% (silt to very fine sand)	difr, foss(py), for(py), from?	yes
ES 06-31	10% (silt)	neo, micenv, phos, difr, pywall, for (py)	yes

Supplementary Table 1, Continued...

Sample	Quartz	Diagenetic Features	Pyrite
ES 06-32	15% (mainly silt)	neo, micbio, phos, difr, pywall, from	yes
ES 06-33	7.5% (silt)	neo, micenv, micbio, phos	yes
ES 06-34	10% (silt)	neo, phos, difr?	yes
ES 06-35	7.5% (silt to very fine sand)	neo, phos, for(py), difr	yes
ES 06-36	7.5-10% (mainly silt)	difr, foss(py), from?	yes
ES 06-37	2.5-5% (silt)	neo, micenv, phos, from?, difr?	yes
ES 06-38	5-7.5% (mainly silt)	micenv, difr, for(py), from?	yes
ES 06-39	~7.5% (mainly silt)	micenv, difr, for(py), from?	yes
ES 06-40	~5% (mainly silt)	neo, micenv, difr, pywall	yes
ES 06-41	~2.5% (silt to very fine sand)	difr, from?	yes
ES 06-42	5% (coarse silt)	neo, micenv, phos, difr, pywall	yes
ES 06-43	15% (silt to very fine sand)	difr, from?	<1%
ES 06-44			
(laminae)	15% (silt to very fine sand)	foss (py), for (py), pywall, difr, from?	~2.5%
ES 06-44	~5 (mainly silt)	foss (py), pywall, difr, from	~2.5%
ES 06-45	~1% (mainly silt)	foss (py), di fr, from?	~2.5%
ES 06-46	~1% (silt)	di fr, foss(py), from?	~1%
ES 06-47	~2.5% (silt to very fine sand)	neo, micenv, difr, from?	yes
ES 06-48	~2.5% (silt)	neo, difr, from?	yes?
ES 06-49	~7.5% (mainly silt)	difr, from?	~2.5%
ES 06-50	~7.5% (silt to very fine sand)	difr, from?	yes
ES 06-51	~7.5% (silt to very fine sand)	neo, micbio, difr	yes
ES 06-52	~5% (mostly very fine sand)	micbio, difr	yes
ES 06-53	~5% (silt to very fine sand)	micbio, difr	yes
ES 08-54	~2.5% (silt)	micbio, neo, dol, pywall, difr	yes
ES 08-55	~2.5% (silt)	micbio, neo, pywall	yes
ES 08-56	<1%	micbio, neo, pywall, for (py)	yes
ES 08-57	~7.5% (silt to very fine sand)	neo, difr, pywall	yes
ES 08-58	<1%	neo, dol, pywall	yes
ES-08-59	~2.5% (silt to very fine sand)	micbio, neo, pywall, difr	yes
ES-08-60	~2.5% (silt to very fine sand)	micenv, micbio, neo, pywall, difr	yes
ES-08-61	~2.5% (silt to very fine sand)	micenv, micbio, neo, pywall, difr	yes
ES-08-61A	~2.5% (silt to very fine sand)	micenv, micbio, neo, pywall, difr	yes
ES-08-62	~1%	micenv, micbio, neo, pywall, difr	yes
ES-08-63	0%	micenv, micbio, neo, pywall, difr	yes
ES-08-64	0%	neo, micbio	no
ES-08-65	0%		no

Supplementary Table 2. *N*-Alkanes and Acyclic Isoprenoids. Sample ES-08-46B

Peak Label	Compound Name	Ret. Time	Area	Height	Area%	Hight%
NC9	Normal Alkane C9					
NC10	Normal Alkane C10					
IP11	Isoprenoid C11					
NC11	Normal Alkane C11	8.585	78	35	0.01	0.01
NC12	Normal Alkane C12	11.264	150	63	0.01	0.02
IP13	Isoprenoid C13	11.651	36	12	0.00	0.00
IP14	Isoprenoid C14	13.275	41	16	0.00	0.00
NC13	Normal Alkane C13	14.025	244	100	0.02	0.03
IP15	Isoprenoid C15	16.129	84	32	0.01	0.01
NC14	Normal Alkane C14	16.748	406	156	0.04	0.05
IP16	Isoprenoid C16	18.402	172	49	0.02	0.01
NC15	Normal Alkane C15	19.376	935	340	0.09	0.10
NC16	Normal Alkane C16	21.890	5731	2248	0.56	0.65
IP18	Isoprenoid C18	23.077	2090	481	0.20	0.14
NC17	Normal Alkane C17	24.292	24541	8936	2.38	2.60
IP19	Isoprenoid C19 (Pristane)	24.434	6839	1665	0.66	0.48
NC18	Normal Alkane C18	26.557	44340	16444	4.31	4.78
IP20	Isoprenoid C20 (Phytane)	26.768	7763	1747	0.75	0.51
NC19	Normal Alkane C19	28.631	58783	22357	5.71	6.50
NC20	Normal Alkane C20	30.544	65538	24643	6.36	7.17
NC21	Normal Alkane C21	32.325	65620	25009	6.37	7.28
NC22	Normal Alkane C22	33.996	61640	23734	5.99	6.91
NC23	Normal Alkane C23	35.575	56051	21578	5.44	6.28
NC24	Normal Alkane C24	37.075	52613	18919	5.11	5.50
NC25	Normal Alkane C25	38.506	47198	17112	4.58	4.98
NC26	Normal Alkane C26	39.876	38645	14343	3.75	4.17
NC27	Normal Alkane C27	41.192	31526	11937	3.06	3.47
NC28	Normal Alkane C28	42.458	25224	9478	2.45	2.76
NC29	Normal Alkane C29	43.680	20266	7717	1.97	2.25
NC30	Normal Alkane C30	44.860	15316	5272	1.49	1.53
NC31	Normal Alkane C31	46.004	11456	3563	1.11	1.04
NC32	Normal Alkane C32	47.185	7308	1810	0.71	0.53
NC33	Normal Alkane C33	48.487	5752	820	0.56	0.24
NC34	Normal Alkane C34	49.952	3312	281	0.32	0.08
NC35	Normal Alkane C35	51.787	1084	88	0.11	0.03
NC36	Normal Alkane C36					
NC37	Normal Alkane C37					
NC38	Normal Alkane C38					
NC39	Normal Alkane C39					
NC40	Normal Alkane C40					

Supplementary Table 3, Definition of *n*-Alkane and Acyclic Isoprenoid Ratios, Sample ES-08-46B

Parameter	Formula
SGC Parameters	
Pristane/Phytane	IP19/IP20
Pristane/nC17	IP19/NC17
Phytane/nC18	IP20/NC18
nC18/nC19	NC18/NC19
nC17/nC29	NC17/NC29
CPI Marzi ⁴	$((NC23+NC25+NC27)+(NC25+NC27+NC29))/(2*(NC24+NC26+NC28))$
Resolved Components (%)	
Normal Paraffins	$100*(NC9+NC10+NC11+NC12+NC13+NC14+NC15+NC16+NC17+NC18+NC19+NC20+NC21+NC22+NC23+NC24+NC25+NC26+NC27+NC28+NC29+NC30+NC31+NC32+NC33+NC34+NC35+NC36+NC37+NC38+NC39+NC40)/TOTAL_RESOLVED$
Isoprenoids	$100*(IP11+IP13+IP14+IP15+IP16+IP18+IP19+IP20)/TOTAL_RESOLVED$

Supplementary Table 4. Saturated Biomarkers, Sample ES-08-46B

Ion	Peak Label	Compound Name	Ret. Time	Area	Height
217	CHOL	<i>5 β cholane (internal standard)</i>			
125	BCAROT	β -carotane			
187	4MDIAM	4-methyldiamantane	9.348	290	103
187	1MDIAM	1-methyldiamantane	9.941	316	107
187	3MDIAM	3-methyldiamantane	10.324	247	85
188	DIAM	diamantane	9.174	212	66
191	TR19	C19 tricyclic terpane	19.003	8930	1773
191	TR20	C20 tricyclic terpane	21.861	15978	2836
191	TR21	C21 tricyclic terpane	25.207	13358	1989
191	TR22	C22 tricyclic terpane	28.588	2391	428
191	TR23	C23 tricyclic terpane	32.831	7837	1317
191	TR24	C24 tricyclic terpane	35.238	3362	553
191	DESAOL	des-A-oleanane			
191	DESALU	des-A-lupane			
191	TR25A	C25 tricyclic terpane (a)	40.311	1002	163
191	TR25B	C25 tricyclic terpane (b)	40.433	1130	162
191	TET24	C24 tetracyclic terpane (TET)	43.554	12667	1956
191	TR26A	C26 tricyclic terpane (a)	44.199	838	119
191	TR26B	C26 tricyclic terpane (b)	44.513	858	117
191	TR28A	C28 tricyclic terpane (a)	53.074	667	104
191	TR28B	C28 tricyclic terpane (b)	53.701	633	83
191	TR29A	C29 tricyclic terpane (a)	55.636	638	114
191	TR29B	C29 tricyclic terpane (b)	56.351	407	133
191	TR30A	C30 tricyclic terpane (a)	60.693	1364	189
191	TR30B	C30 tricyclic terpane (b)	61.390	765	116
191	TS	Ts 18 α (H)-trisnorhopane	57.798	6438	982
191	TM	Tm 17 α (H)-trisnorhopane	59.437	13801	2031
191	H28	C28 17 α 18 α 21 β (H)-bisnorhopane			
191	NOR25H	C29 Nor-25-hopane			
191	H29	C29 Tm 17 α (H)21 β (H)-norhopane	65.191	23299	3420
191	C29TS	C29 Ts 18 α (H)-norneohopane	65.452	5198	741
191	DH30	C30 17 α (H)-diahopane	66.202	9303	1414
191	M29	C29 normoretane	67.196	3731	512
191	OLA	oleanane a			
191	OLB	oleanane b			
191	H30	C30 17 α (H)-hopane	68.660	32495	4831
191	C30TS	C29 Ts 18 α (H)-norneohopane	69.462	1966	287
191	M30	C30 moretane	70.212	5649	797

191	H31S	C31 22S 17 α (H) hopane	72.705	17390	2612
191	H31R	C31 22R 17 α (H) hopane	73.211	12674	1809
191	GAM	gammacerane	73.647	6991	849
191	H32S	C32 22S 17 α (H) hopane	75.931	12272	1845
191	H32R	C32 22R 17 α (H) hopane	76.611	8442	1255
191	H33S	C33 22S 17 α (H) hopane	79.644	5315	754
191	H33R	C33 22R 17 α (H) hopane	80.586	4050	517
191	H34S	C34 22S 17 α (H) hopane	83.480	2715	394
191	H34R	C34 22R 17 α (H) hopane	84.613	1932	276
191	H35S	C35 22S 17 α (H) hopane	87.194	1594	208
191	H35R	C35 22R 17 α (H) hopane	88.484	1228	159

Steranes					
217	S21	C21 sterane	29.163	3337	489
217	S22	C22 sterane	33.878	1075	155
217	DIA27S	C27 $\beta\alpha$ 20S diasterane	48.558	1168	182
217	DIA27R	C27 $\beta\alpha$ 20R diasterane	50.092	804	127
217	DIA28SA	C28 $\beta\alpha$ 20S diasterane a	52.341	623	90
217	DIA28SB	C28 $\beta\alpha$ 20S diasterane b	52.603	958	113
217	DIA28RA	C28 $\beta\alpha$ 20R diasterane a	54.067	724	81
217	DIA28RB	C28 $\beta\alpha$ 20R diasterane b	54.207	417	70
217	C27S	C27 $\alpha\alpha$ 20S sterane	55.253	1057	139
217	BB_D29S	C27 $\beta\beta$ 20R + C29 dia20S	55.915	2258	153
217	C27BBS	C27 $\beta\beta$ 20S sterane	56.160	1452	146
217	C27R	C27 $\alpha\alpha$ 20R sterane	57.031	1502	202
217	DIA29R	C29 $\beta\alpha$ 20R diasterane	57.607	1214	135
217	C28S	C28 $\alpha\alpha$ 20S sterane	59.402	1112	102
217	C28BBR	C28 $\beta\beta$ 20R sterane(+5 baa)	60.047	797	88
217	C28BBS	C28 $\beta\beta$ 20S sterane	60.449	1040	123
217	C28R	C28 $\alpha\alpha$ 20R sterane	61.634	1214	107
217	C29S	C29 $\alpha\alpha$ 20S sterane	62.820	697	102
217	C29BBR	C29 $\beta\beta$ 20R sterane(+5 baa)	63.657	1567	177
217	C29BBS	C29 $\beta\beta$ 20S sterane	63.953	1407	150
217	C29R	C29 $\alpha\alpha$ 20R sterane	65.383	1620	139
218	C27ABBR	C27 $\beta\beta$ 20R sterane	55.741	1342	192
218	C27ABBS	C27 $\beta\beta$ 20S sterane	56.142	1147	171
218	C28ABBR	C28 $\beta\beta$ 20R sterane	60.047	922	112
218	C28ABBS	C28 $\beta\beta$ 20S sterane	60.466	1041	128
218	C29ABBR	C29 $\beta\beta$ 20R sterane	63.657	1516	189
218	C29ABBS	C29 $\beta\beta$ 20S sterane	63.988	1469	179
218	C30ABBR	C30 $\beta\beta$ 20R sterane	66.673	203	33
218	C30ABBS	C30 $\beta\beta$ 20S sterane	66.899	151	27
259	D27S	C27 $\beta\alpha$ 20S diasterane	48.540	771	114
259	D27R	C27 $\beta\alpha$ 20R diasterane	50.075	445	76

259	D28SA	C28 $\beta\alpha$ 20S diasterane a	52.341	336	52
259	D28SB	C28 $\beta\alpha$ 20S diasterane b	52.620	581	70
259	D28RA	C28 $\beta\alpha$ 20R diasterane a	54.032	532	66
259	D28RB	C28 $\beta\alpha$ 20R diasterane b	54.242	334	44
259	D29S	C29 $\beta\alpha$ 20S diasterane	55.881	1303	107
259	D29R	C29 $\beta\alpha$ 20R diasterane	57.624	860	75
259	C30TP1	C30 tetracyclic polyprenoid	67.178	1494	205
259	C30TP2	C30 tetracyclic polyprenoid	67.318	1336	212

Miscellaneous Ratios	By Areas	By Heights
Terpanes (m/z 191)		
C19/C23 Tricyclic terpanes	1.14	1.35
C22/C21 Tricyclic terpanes	0.18	0.22
C22/C24 Tricyclic terpanes	0.71	0.77
C23/C24 Tricyclic terpanes	2.33	2.38
C24/C23 Tricyclic terpanes	0.43	0.42
C26/C25 Tricyclic terpanes	0.80	0.73
C24 Tetracyclic/C23 Tricyclic	1.62	1.49
C24 Tetracyclic/C26 Tricyclics	7.47	8.29
(C28+C29 Tricyclics)/Ts	0.36	0.44
Ts/Tm trisnorhopanes	0.47	0.48
Ts/(Ts+Tm) trisnorhopanes	0.32	0.33
25-nor-hopane/hopane		
C29Ts/C29 Hopane	0.22	0.22
C29Ts/(C29TS+C29) Hopane	0.18	0.18
C23 Tricyclic/Hopane	0.24	0.27
C24 Tetracyclic/Hopane	0.39	0.40
Bisnorhopane/Hopane		
Norhopane/Hopane	0.72	0.71
Diahopane/Hopane	0.29	0.29
Oleanane/Hopane		
Moretane/Hopane	0.17	0.16
Moretane/(Moretane+Hopane)	0.15	0.14
C30Ts/C30 Hopane	0.06	0.06
Gammacerane/Hopane	0.22	0.18
C32 S/(S+R) Homohopanes	0.59	0.60
Gammacerane/H31R Homohopane	0.55	0.47
C35/C34 Homohopanes	0.61	0.55
C35/C34 S Homohopanes	0.59	0.53
C35 Homohopane Index	0.04	0.04
Rel % C31 Homohopane	44.5	45.0
Rel % C32 Homohopane	30.6	31.5

Rel % C33Homohopane	13.9	12.9
Rel % C34 Homohopane	6.9	6.8
Rel % C35 Homohopane	4.2	3.7

Miscellaneous Ratios	By Areas	By Heights
Steranes (m/z 217; 218)		
%C27 $\alpha\alpha\alpha$ R (217)	34.6	45.1
%C28 $\alpha\alpha\alpha$ R (217)	28.0	23.9
%C29 $\alpha\alpha\alpha$ R (217)	37.4	31.0
S/R (C ₂₉ $\alpha\alpha\alpha$) (217)	0.43	0.73
S/(S+R) (C ₂₉ $\alpha\alpha\alpha$) (217)	0.30	0.42
$\beta\beta/(\alpha\alpha+\beta\beta)$ (C ₂₉) (217)	0.56	0.58
$\beta\beta S/(\alpha\alpha R+\beta\beta S)$ (C ₂₉) (217)	0.46	0.52
$\alpha\beta\beta S/\alpha\alpha\alpha R$ (C ₂₉) (217)	0.87	1.08
(C ₂₁ +C ₂₂)/(C ₂₇ +C ₂₈ +C ₂₉) (217)	0.20	0.27
Diaster/ $\alpha\alpha\alpha$ Ster (C ₂₇) (217)	0.77	0.91
Diaster/(Diaster+ $\alpha\alpha\alpha$) Ster (C ₂₇) (217)	0.44	0.48
%C27 $\alpha\beta\beta S$ (218)	31.4	35.8
%C28 $\alpha\beta\beta S$ (218)	28.5	26.8
%C29 $\alpha\beta\beta S$ (218)	40.2	37.4
%C27 $\alpha\beta\beta$ (R+S) (218)	33.5	37.4
%C28 $\alpha\beta\beta$ (R+S) (218)	26.4	24.7
%C29 $\alpha\beta\beta$ (R+S) (218)	40.1	37.9
C30 $\alpha\beta\beta S$ Sterane Index (218)	4.0	5.3
C30 S+R Sterane Index (218)	4.5	5.8
C ₂₇ /C ₂₉ ($\alpha\beta\beta S$) (218)	0.78	0.96
C ₂₈ /C ₂₉ ($\alpha\beta\beta S$) (218)	0.71	0.72
C ₂₉ /C ₂₇ ($\alpha\beta\beta S$) (218)	1.28	1.05
C ₂₉ /C ₂₇ ($\alpha\beta\beta$) (218)	1.20	1.01
Various (m/z 191; 217)		
Steranes/Hopanes	0.14	0.10
Tricyclic terpanes/Hopanes	0.38	0.43
Tricyclic terpanes/Steranes	2.78	4.20
Tricyclic/Pentacyclic Terpanes	41.3	47.3
Steranes/Terpanes	0.10	0.08
% Tricyclic Terpanes	26.6	29.8
% Pentacyclic Terpanes	64.38	29.76
% Steranes	9.1	7.3

Supplementary Table 5, Definition of Saturated Biomarker Ratios, Sample ES-08-46B

Parameter	Formula
Terpanes (<i>m/z</i> 191)	
C19/C23 Tricyclic terpanes	TR19/TR23
C22/C21 Tricyclic terpanes	TR22/TR21
C22/C24 Tricyclic terpanes	TR22/TR24
C23/C24 Tricyclic terpanes	TR23/TR24
C24/C23 Tricyclic terpanes	TR24/TR23
C26/C25 Tricyclic terpanes	(TR26A+TR26B)/(TR25A+TR25B)
C24 Tetracyclic/C23 Tricyclic	TET24/TR23
C24 Tetracyclic/C26 Tricyclics	TET24/(TR26A+TR26B)
(C28+C29 Tricyclics)/Ts	(TR28A+TR28B+TR29A+TR29B)/TS
Ts/Tm trisnorhopanes	TS/TM
Ts/(Ts+Tm) trisnorhopanes	TS/(TS+TM)
25- <i>nor</i> -hopane/hopane	NOR25H/H30
C29Ts/C29 Hopane	C29TS/H29
C29Ts/(C29TS+C29) Hopane	C29Ts/(C29TS+H29)
C23 Tricyclic/Hopane	TR23/H30
C24 Tetracyclic/Hopane	TET24/H30
Bisnorhopane/Hopane	H28/H30
Norhopane/Hopane	H29/H30
Diahopane/Hopane	DH30/H30
Oleanane/Hopane	(OLA+OLB)/H30
Moretane/Hopane	M30/H30
Moretane/(Moretane+Hopane)	M30/(M30+H30)
C30Ts/C30 Hopane	C30TS/H30
Gammacerane/Hopane	GAM/H30
C32 S/(S+R) Homohopanes	H32S/(H32R+H32S)
Gam/H31R Homohopane	GAM/H31R
C35/C34 Homohopanes	(H35R+H35S)/(H34R+H34S)
C35/C34 S Homohopanes	H35S/H34S
C35 Homohopane Index	(H35S+H35R)/(H31S+H31R+H32S+H32R+H33S+H33R+H34S+H34R+H35S+H35R)
Rel % C31 Homohopane	100*(H31S+H31R)/(H31S+H31R+H32S+H32R+H33S+H33R+H34S+H34R+H35S+H35R)
Rel % C32 Homohopane	100*(H32S+H32R)/(H31S+H31R+H32S+H32R+H33S+H33R+H34S+H34R+H35S+H35R)
Rel % C33 Homohopane	100*(H33S+H33R)/(H31S+H31R+H32S+H32R+H33S+H33R+H34S+H34R+H35S+H35R)
Rel % C34 Homohopane	100*(H34S+H34R)/(H31S+H31R+H32S+H32R+H33S+H33R+H34S+H34R+H35S+H35R)
Rel % C35 Homohopane	100*(H35S+H35R)/(H31S+H31R+H32S+H32R+H33S+H33R+H34S+H34R+H35S+H35R)
Steranes (<i>m/z</i> 217; 218)	
%C ₂₇ αααR (217)	100*C27R/(C27R+C28R+C29R)
%C ₂₈ αααR (217)	100*C28R/(C27R+C28R+C29R)
%C ₂₉ αααR (217)	100*C29R/(C27R+C28R+C29R)

S/R (C ₂₉ ααα) (217)	C29S/C29R
S/(S+R) (C ₂₉ ααα) (217)	C29S/(C29S+C29R)
ββ/(αα+ββ) (C ₂₉) (217)	(C29BBR+C29BBS)/(C29S+C29BBR+C29BBS+C29R)
ββS/(ααR+ββS) (C ₂₉) (217)	(C29BBS+C29BBS)/(C29R+C29BBS+C29BBS+C29R)
αββS/αααR (C ₂₉) (217)	C29BBS/C29R
(C ₂₁ +C ₂₂)/(C ₂₇ +C ₂₈ +C ₂₉) (217)	(S21+S22)/(DIA27S+DIA27R+DIA28SA+DIA28SB+DIA28RA+DIA28RB+C27S+BB_D29S+C27BBS+C27R+ DIA29R+C28S+C28BBR+C28BBS+C28R+C29S+C29BBR+C29BBS+C29R)
Diaster/ααα Ster (C ₂₇) (217)	(DIA27S+DIA27R)/(C27S+C27R)
Dia/(Dia+ααα) Ster (C ₂₇)	(DIA27S+DIA27R)/(DIA27S+DIA27R+C27S+C27R)
C ₂₇ /C ₂₉ (αββS) (218)	C27ABBS/C29ABBS
C ₂₈ /C ₂₉ (αββS) (218)	C28ABBS/C29ABBS
C ₂₉ /C ₂₇ (αββS) (218)	C29ABBS/C27ABBS
Diaster/ααα Ster (C ₂₇) (217)	(DIA27S+DIA27R)/(C27S+C27R)
C30 αββS Sterane Index (218)	100*(C30ABBS)/(C27ABBS+C28ABBS+C29ABBS+C30ABBS)
C30 S+R Sterane Index (218)	100*(C30ABBR+C30ABBS)/(C27ABBR+C27ABBS+C28ABBR+C28ABBS+C29ABBR+C29ABBS+ C30ABBR+C30ABBS)
%C ₂₇ αββS (218)	100*C27ABBS/(C27ABBS+C28ABBS+C29ABBS)
%C ₂₈ αββS (218)	100*C28ABBS/(C27ABBS+C28ABBS+C29ABBS)
%C ₂₉ αββS (218)	100*C29ABBS/(C27ABBS+C28ABBS+C29ABBS)
%C ₂₇ αββ (R+S) (218)	100*(C27ABBR+C27ABBS)/(C27ABBR+C27ABBS+C28ABBR+C28ABBS+C29ABBR+C29ABBS)
%C ₂₈ αββ (R+S) (218)	100*(C28ABBR+C28ABBS)/(C27ABBR+C27ABBS+C28ABBR+C28ABBS+C29ABBR+C29ABBS)
%C ₂₉ αββ (R+S) (218)	100*(C29ABBR+C29ABBS)/(C27ABBR+C27ABBS+C28ABBR+C28ABBS+C29ABBR+C29ABBS)
C30 αββS Sterane Index (218)	100*(C30ABBS)/(C27ABBS+C28ABBS+C29ABBS+C30ABBS)
C30 S+R Sterane Index (218)	100*(C30ABBR+C30ABBS)/(C27ABBR+C27ABBS+C28ABBR+C28ABBS+C29ABBR+C29ABBS+ C30ABBR+C30ABBS)
C ₂₇ /C ₂₉ (αββS) (218)	C27ABBS/C29ABBS
C ₂₈ /C ₂₉ (αββS) (218)	C28ABBS/C29ABBS
C ₂₉ /C ₂₇ (αββS) (218)	C29ABBS/C27ABBS
C ₂₉ /C ₂₇ (αββ) (218)	(C29ABBR+C29ABBS)/(C27ABBR+C27ABBS)
Various (m/z 191; 217)	
Steranes/Hopanes	(DIA27S+DIA27R+DIA28SA+DIA28SB+DIA28RA+DIA28RB+C27S+BB_D29S+C27BBS+C27R+DIA29R+ C28S+C28BBR+C28BBS+C28R+C29S+C29BBR+C29BBS+C29R)/(TS+TM+H28+H29+C29TS+DH30+H30+ H31R+H31S+H32R+H32S+H33R+H33S+H34R+H34S+H35R+H35S)
Tricyclic terpanes/Hopanes	(TR19+TR20+TR21+TR22+TR23+TR24+TR25A+TR25B+TR26A+TR26B+TR28A+TR28B+TR29A+TR29B+TR30A+TR30B)/(TS+TM+H28+H29+C29TS+DH30+H30+ C30TS+H31R+H31S+H32R+H32S+H33R+H33S+ H34R+ H34S+H35R+H35S)
Tricyclic terpanes/Steranes	(TR19+TR20+TR21+TR22+TR23+TR24+TR25A+TR25B+TR26A+TR26B+TR28A+TR28B+TR29A+TR29B+TR30A+TR30B)/(DIA27S+DIA27R+DIA28SA+DIA28SB+DIA28RA+DIA28RB+C27S+BB_D29S+C27BBS+ C27R+DIA29R+C28S+C28BBR+C28BBS+C28R+C29S+C29BBR+C29BBS+C29R)

Tricyclic/Pentacyclic Terpanes	$100 * (TR19 + TR20 + TR21 + TR22 + TR23 + TR24 + TR25A + TR25B + TET24 + TR26A + TR26B + TR28A + TR28B + TR29A + TR29B + TR30A + TR30B) / (TS + TM + H28 + NOR25H + H29 + C29TS + DH30 + M29 + OLA + OLB + H30 + C30TS + M30 + H31S + H31R + GAM + H32S + H32R + H33S + H33R + H34S + H34R + H35S + H35R)$
Steranes/Terpanes	$(S21 + S22 + DIA27S + DIA27R + DIA28SA + DIA28SB + DIA28RA + DIA28RB + C27S + BB_D29S + C27BBS + C27R + C28S + C28BBR + C28BBS + C28R + C29S + C29BBR + C29BBS + C29R) / (TR19 + TR20 + TR21 + TR22 + TR23 + TR24 + TR25A + TR25B + TET24 + TR26A + TR26B + TR28A + TR28B + TR29A + TR29B + TR30A + TR30B + TS + TM + H28 + NOR25H + H29 + C29TS + DH30 + M29 + OLA + OLB + H30 + C30TS + M30 + H31S + H31R + GAM + H32S + H32R + H33S + H33R + H34S + H34R + H35S + H35R)$
% Tricyclic Terpanes	$100 * (TR19 + TR20 + TR21 + TR22 + TR23 + TR24 + TR25A + TR25B + TET24 + TR26A + TR26B + TR28A + TR28B + TR29A + TR29B + TR30A + TR30B) / ((TR19 + TR20 + TR21 + TR22 + TR23 + TR24 + TR25A + TR25B + TET24 + TR26A + TR26B + TR28A + TR28B + TR29A + TR29B + TR30A + TR30B + TS + TM + H28 + NOR25H + H29 + C29TS + DH30 + M29 + OLA + OLB + H30 + C30TS + M30 + H31S + H31R + GAM + H32S + H32R + H33S + H33R + H34S + H34R + H35S + H35R) + (S21 + S22 + DIA27S + DIA27R + DIA28SA + DIA28SB + DIA28RA + DIA28RB + C27S + BB_D29S + C27BBS + C27R + C28S + C28BBR + C28BBS + C28R + C29S + C29BBR + C29BBS + C29R))$
% Pentacyclic Terpanes	$100 * (TS + TM + H28 + NOR25H + H29 + C29TS + DH30 + M29 + OLA + OLB + H30 + C30TS + M30 + H31S + H31R + GAM + H32S + H32R + H33S + H33R + H34S + H34R + H35S + H35R) / ((TR19 + TR20 + TR21 + TR22 + TR23 + TR24 + TR25A + TR25B + TET24 + TR26A + TR26B + TR28A + TR28B + TR29A + TR29B + TR30A + TR30B + TS + TM + H28 + NOR25H + H29 + C29TS + DH30 + M29 + OLA + OLB + H30 + C30TS + M30 + H31S + H31R + GAM + H32S + H32R + H33S + H33R + H34S + H34R + H35S + H35R) + (S21 + S22 + DIA27S + DIA27R + DIA28SA + DIA28SB + DIA28RA + DIA28RB + C27S + BB_D29S + C27BBS + C27R + C28S + C28BBR + C28BBS + C28R + C29S + C29BBR + C29BBS + C29R))$
% Steranes	$100 * (S21 + S22 + DIA27S + DIA27R + DIA28SA + DIA28SB + DIA28RA + DIA28RB + C27S + BB_D29S + C27BBS + C27R + C28S + C28BBR + C28BBS + C28R + C29S + C29BBR + C29BBS + C29R) / ((TR19 + TR20 + TR21 + TR22 + TR23 + TR24 + TR25A + TR25B + TET24 + TR26A + TR26B + TR28A + TR28B + TR29A + TR29B + TR30A + TR30B + TS + TM + H28 + NOR25H + H29 + C29TS + DH30 + M29 + OLA + OLB + H30 + C30TS + M30 + H31S + H31R + GAM + H32S + H32R + H33S + H33R + H34S + H34R + H35S + H35R) + (S21 + S22 + DIA27S + DIA27R + DIA28SA + DIA28SB + DIA28RA + DIA28RB + C27S + BB_D29S + C27BBS + C27R + C28S + C28BBR + C28BBS + C28R + C29S + C29BBR + C29BBS + C29R))$

Supplementary Table 6, List of Aromatic Compounds, Sample ES-08-46B

Ion	Peak Label	Compound Name	Ret. Time	Area	Height	ppm (Area)
230	OTP	<i>Ortho-terphenyl</i> (internal standard)	75.030	63920	15142	300.0
128	NAPH	Naphthalene				
142	2MN	2-Methylnaphthalene	38.012	696	107	3.3
142	1MN	1-Methylnaphthalene	39.242	648	110	3.0
154	BP	Biphenyl	44.735	875	130	4.1
156	2EN	2-Ethyl-naphthalene	46.184	260	47	1.2
156	1EN	1-Ethyl-naphthalene	46.285	177	35	0.8
156	26DMN	2,6-Dimethylnaphthalene	47.077	1395	215	6.5
156	27DMN	2,7-Dimethylnaphthalene	47.229	1409	212	6.6
156	1317DMN	1,3 & 1,7-Dimethylnaphthalenes	48.223	4232	549	19.9
156	16DMN	1,6-Dimethylnaphthalene	48.492	3132	502	14.7
156	23DMN	2,3-Dimethylnaphthalene	49.655	499	128	2.3
156	14DMN	1,4-Dimethylnaphthalene	49.756	2538	330	11.9
156	15DMN	1,5-Dimethylnaphthalene	49.874	801	232	3.8
156	12DMN	1,2-Dimethylnaphthalene	50.818	1103	174	5.2
168	2MBP	2-Methylbiphenyl				
168	DPM	Diphenylmethane				
168	3MBP	3-Methylbiphenyl	53.345	623	94	2.9
168	4MBP	4-Methylbiphenyl	54.002	338	55	1.6
168	DBF	Dibenzofuran	55.434	1756	264	8.2
170	BB_EMN	Ethyl-methyl-Naphthalene	55.165	2646	337	12.4
170	AB_EMN	Ethyl-methyl-Naphthalene	56.361	1494	223	7.0
170	137TMN	1,3,7-Trimethylnaphthalene	56.816	6797	1130	31.9
170	136TMN	1,3,6-Trimethylnaphthalene	57.187	12462	2089	58.5
170	146135T	(1,4,6+1,3,5)-Trimethylnaphthalenes	58.248	9021	1472	42.3
170	236TMN	2,3,6-Trimethylnaphthalene	58.518	14067	2404	66.0
170	127TMN	1,2,7-Trimethylnaphthalene	59.259	2321	388	10.9
170	167126T	(1,6,7+1,2,6)-Trimethylnaphthalenes	59.444	16504	2398	77.5
170	124TMN	1,2,4-Trimethylnaphthalene	60.354	1129	199	5.3
170	125TMN	1,2,5-Trimethylnaphthalene	60.792	6944	1195	32.6
178	PHEN	Phenanthrene	70.329	1256253	249017	5896.1
184	1357	1,3,5,7-Tetramethylnaphthalene	64.769	9188	1572	43.1
184	1367	1,3,6,7-Tetramethylnaphthalene	65.914	20840	4270	97.8
184	1247	(1,2,4,7+1,2,4,6+1,4,6,7)-Tetramethylnaphthalenes	66.656	8481	1613	39.8
184	1257	1,2,5,7-Tetramethylnaphthalene	66.841	8923	1834	41.9
184	2367	2,3,6,7-Tetramethylnaphthalene	67.212	7191	1513	33.8
184	1267	1,2,6,7-Tetramethylnaphthalene	67.650	10587	2199	49.7
184	1237	1,2,3,7-Tetramethylnaphthalene	67.835	2010	423	9.4
184	1236	1,2,3,6-Tetramethylnaphthalene	68.105	5344	1090	25.1
184	1256	1,2,5,6-Tetramethylnaphthalene	68.813	16494	3532	77.4
184	DBT	Dibenzothiophene	69.032	112118	21663	526.2
191	BH32	C32 Benzohopane				
191	BH33	C33 Benzohopane				

191	BH34	C34 Benzohopane				
191	BH35	C35 Benzohopane				
192	3MP	3-Methylphenanthrene	75.249	552537	109695	2593.3
192	2MP	2-Methylphenanthrene	75.434	649060	137671	3046.3
192	9MP	9-Methylphenanthrene	76.142	796280	156957	3737.2
192	1MP	1-Methylphenanthrene	76.310	672063	141663	3154.2
198	CAD	Cadalene	66.268	437	91	2.1
198	4MDBT	4 Methyl Dibenzothiophene	73.581	73259	15363	343.8
198	23MDBT	2 & 3 Methyl Dibenzothiophenes	74.356	61890	12866	290.5
198	1MDBT	1 Methyl Dibenzothiophene	75.165	26439	5119	124.1
206	36DMP	3,6-Dimethylphenanthrene	79.477	85973	17208	403.5
206	26DMP	2,6-Dimethylphenanthrene	79.730	160647	35367	754.0
206	27DMP	2,7-Dimethylphenanthrene	79.831	117871	24344	553.2
206	39DMP	(3,9+3,10+2,10+1,3)- Dimethylphenanthrenes	80.354	620473	111436	2912.1
206	29DMP	(2,9+1,6)-Dimethylphenanthrenes	80.556	341191	52780	1601.3
206	17DMP	1,7-Dimethylphenanthrene	80.707	287738	61311	1350.5
206	23DMP	2,3-Dimethylphenanthrene	80.977	166821	34867	783.0
206	19DMP	1,9-Dimethylphenanthrene	81.078	163525	38672	767.5
206	18DMP	1,8-Dimethylphenanthrene	81.500	93697	19330	439.8
206	12DMP	1,2-Dimethylphenanthrene	82.005	84401	18508	396.1
231	231A20	C20 Triaromatic Steroid	92.354	14452	2965	67.8
231	231B21	C21 Triaromatic	94.849	8937	1489	41.9
231	231C26	C26 20S Triaromatic	104.051	1502	286	7.0
231	231D26	C27 20S & C26 20R Triaromatic	105.653	2495	444	11.7
231	TADMD1	C28 23,24-Cholestane Triaromatic				
231	TADMD2	C28 23,24-Cholestane Triaromatic				
231	231E28	C28 20S Triaromatic	106.950	1620	235	7.6
231	231F27	C27 20R Triaromatic	107.608	862	187	4.0
231	TADMD3	C28 23,24-Cholestane Triaromatic				
231	C29TA1	C29 Triaromatic				
231	C29TA2	C29 Triaromatic				
231	TADMD4	C28 23,24-Cholestane Triaromatic				
231	231G28	C28 20R Triaromatic	109.209	1582	262	7.4
231	TADMD5	C28 23,24-Cholestane Triaromatic				
231	C29TA3	C29 Triaromatic				
245	C3S	C27 20S 3-Methyl Triaromatic Steroid	106.731	496	105	2.3
245	C4S	C27 20S 4-Methyl Triaromatic Steroid	107.372	493	119	2.3
245	E2S	C28 20S 2-Methyl Triaromatic Steroid	107.962	503	94	2.4
245	E3SC3R	C28 20S 3-Methyl & C27 20R 3-Methyl TAS	108.282	1242	218	5.8
245	E4SC4R	C28 20S 4-Methyl & C27 20R 4-Methyl TAS	108.855	1275	174	6.0
245	S2S	C29 20S 2-Methyl Triaromatic Steroid	109.057	530	91	2.5
245	DA	Triaromatic Dinosteroid a	109.276	470	134	2.2
245	S3S	C29 20S 3-Methyl Triaromatic Steroid	109.445	971	134	4.6
245	DB	Triaromatic Dinosteroid b	109.883	1329	240	6.2
245	S4SE2R	C29 20S 4-Methyl & C28 20R 2-Methyl TAS	110.068	2083	284	9.8

245	E3R	C28 20R 3-Methyl Triaromatic Steroid	110.203	513	158	2.4
245	E4R	C28 20R 4-Methyl Triaromatic Steroid	110.810	1127	164	5.3
245	DC	Triaromatic Dinosteroid c	110.995	1345	313	6.3
245	DD	Triaromatic Dinosteroid d	111.097	1212	208	5.7
245	S2R	C29 20R 2-Methyl Triaromatic Steroid	111.518	597	102	2.8
245	S3R	C29 20R 3-Methyl Triaromatic Steroid	111.720	1054	165	4.9
245	DE	Triaromatic Dinosteroid e	111.922	1532	192	7.2
245	S4R	C29 20R 4-Methyl Triaromatic Steroid	112.361	456	115	2.1
245	DF	Triaromatic Dinosteroid f	112.462	1320	230	6.2
253	S253A	C21 Ring-C Monoaromatic Steroid	84.550	650	69	3.1
253	S253B	C22 Monoaromatic steroid	87.028	191	42	0.9
253	S253C	C27 Reg 5 β (H),10 β (CH3) 20S				
253	S253D	C27 Dia 10 β (H),5 β (CH3) 20S				
253	S253E	C27 Dia10 β H,5 β CH3 20R+Reg5 β H,10 β CH3 20R				
253	S253F	C27 Reg 5 α (H),10 β (CH3) 20S				
253	S253G	C28 Dia 10 α H,5 α CH3 20s+Reg5 β H,10 β CH3 20S				
253	S253H	C27 Reg 5 α (H),10 β (CH3) 20R				
253	S253I	C28 Reg 5 α (H),10 β (CH3) 20S				
253	S253J	C28 Dia 10 α H,5 α CH3 20R+Reg5 β H,10 β CH3 20R				
253	S253K	C29 Dia 10 β H,5 β CH3 20S+Reg5 β H,10 β CH3 20S				
253	S253L	C29 Reg 5 α (H),10 β (CH3) 20S				
253	S253M	C28 Reg 5 α (H),10 β (CH3) 20R				
253	S253N	C29 Dia 10 β H,5 β CH3 20R+Reg5 β H,10 β CH3 20R				
253	S253O	C29 Reg 5 α (H),10 β (CH3) 20R				
365	SH29	C29 8,14-secohopanoids	104.152	2437	389	11.4
365	SH30	C30 8,14-secohopanoids	106.108	1818	350	8.5

Miscellaneous Ratios

By Heights

Triaromatic Steroids m/z 231

(C20+C21)/S TAS	0.76
TAS #1 20/20+27	0.94
TAS #2 21/21+28	0.85
%26TAS	38.9
%27TAS	25.4
%28TAS	35.6
%29TAS	
C28/C26 20S TAS	0.82
C28/C27 20R TAS	1.40

Monoaromatic Steroids m/z 253

Dia/Regular C27 MAS	
%27 MAS	
%28 MAS	

%29 MAS	
(C21+C22)/S MAS	1.00
TAS/(MAS+TAS)	0.98
TA28/(TA28+MA29)	1.00
TriaromaticMethylsteroids	
m/z 245	
Dinosteroid Index	0.41
C4/C3+C4 Mester	0.48
Phenanthrenes and Naphthalenes	
MPI-1	0.68
MPI-2	0.75
MPI-3	0.83
Rc(a) if Ro < 1.3 (Ro%)	0.78
Rc(b) if Ro > 1.3 (Ro%)	1.89
DNR-1	1.84
DNR-2	0.93
TNR1	1.63
TDE-1	6.01
TDE-2	0.16
MDR	3.00
Rm (Ro%)	0.75
MDR23	0.59
MDR1	0.24
DBT/Phenanthrene	0.09

Supplementary Table 7, Definition of Aromatic Compounds Ratios, Sample ES-08-46B

Parameter	Formula
Mono- (MAS) and Triaromatic Steroids (TAS)	
(C20+C21)/S TAS	$(231A20+231B21)/(231A20+231B21+231C26+231D26+231E28+231F27+231G28+C29TA3)$
TAS #1 20/20+27	$(231A20)/(231A20+231F27)$
TAS #2 21/21+28	$(231B21)/(231B21+231G28)$
%26 TAS	$100*(231C26)/(231C26+231F27+231G28+C29TA3)$
%27 TAS	$100*(231F27)/(231C26+231F27+231G28+C29TA3)$
%28 TAS	$100*(231G28)/(231C26+231F27+231G28+C29TA3)$
%29 TAS	$100*(C29TA3)/(231C26+231F27+231G28+C29TA3)$
C28/C26 20S TAS	$(231E28)/(231C26)$
C28/C27 20R TAS	$(231G28)/(231F27)$
Dia/Regular C27 MAS	$(S253D)/(S253C)$
%27 MAS	$100*(S253C+S253D+S253E+S253F+S253H)/(S253C+S253D+S253E+S253F+S253G+S253H+S253I+S253J+S253K+S253L+S253M+S253N+S253O)$
%28 MAS	$100*(S253G+S253I+S253J+S253M)/(S253C+S253D+S253E+S253F+S253G+S253H+S253I+S253J+S253K+S253L+S253M+S253N+S253O)$
%29 MAS	$100*(S253K+S253L+S253N+S253O)/(S253C+S253D+S253E+S253F+S253G+S253H+S253I+S253J+S253K+S253L+S253M+S253N+S253O)$
(C21+C22)/S MAS	$(S253A+S253B)/(S253A+S253B+S253C+S253D+S253E+S253F+S253G+S253H+S253I+S253J+S253K+S253L+S253M+S253N+S253O)$
TAS/(MAS+TAS)	$(231A20+231B21+231C26+231D26+231E28+231F27+231G28+C29TA3)/((231A20+231B21+231C26+231D26+231E28+231F27+231G28+C29TA3)+(S253A+S253B+S253C+S253D+S253E+S253F+S253G+S253H+S253I+S253J+S253K+S253L+S253M+S253N+S253O))$
TA28/(TA28+MA29)	$(231E28+231G28)/(231E28+231G28+S253K+S253L+S253N+S253O)$
Triaromatic Methylsteroids	
Dinosteroid Index	$(DA+DB+DC+DD+DE+DF)/(C3S+C4S+E2S+E3SC3R+E4SC4R+S2S+DA+S3S+DB+S4SE2R+E3R+E4R+DC+DD+S2R+S3R+DE+S4R+DF)$
C4/C3+C4 Mester	$(C4S+E4R+S4R)/(C3S+C4S+E3R+E4R+S3R+S4R)$
Phenanthrenes, Naphthalenes, and Dibenzothiophenes	
MPI-1	$(1.5*(3MP+2MP))/(PHEN+9MP+1MP)$
MPI-2	$(3*(2MP))/(PHEN+9MP+1MP)$
MPI-3	$(3MP+2MP)/(9MP+1MP)$
Rc(a) if Ro < 1.3 (Ro%)	$((.6)*(1.5*(2MP+3MP))/(PHEN+9MP+1MP))+.37)$
Rc(b) if Ro > 1.3 (Ro%)	$((-.6)*(1.5*(2MP+3MP))/(PHEN+9MP+1MP))+2.3)$
DNR-1	$(26DMN+27DMN)/(15DMN)$
DNR-2	$(26DMN+27DMN)/(14DMN+23DMN)$
TNR1	$(236TMN)/(146135T)$
TDE-1	$(125TMN)/(124TMN)$

Supplementary Table 7, Definition of Aromatic Compounds Ratios, Sample ES-08-46B

TDE-2	$(127\text{TMN})/(167126\text{T})$
MDR	$(4\text{MDBT})/(1\text{MDBT})$
Rm (Ro%)	$(0.40+0.30*(4\text{MDBT}/1\text{MDBT})-0.094*(4\text{MDBT}/1\text{MDBT})*(4\text{MDBT}/1\text{MDBT})+0.011*(4\text{MDBT}/1\text{MDBT})*(4\text{MDBT}/1\text{MDBT})*(4\text{MDBT}/1\text{MDBT}))$
MDR23	$(23\text{MDBT})/(\text{DBT})$
MDR1	$(1\text{MDBT})/(\text{DBT})$
DBT/Phenanthrene	$(\text{DBT})/(\text{PHEN})$

Supplementary Table 8. Major, minor and trace elements concentrations (all are LA-ICP-MS analyses). Interpretations are based on values below 15% of relative standard deviation (RSD).

Sample name	Mg	Al	Si	P	Ca	Ti47	Ti49
ES-06-30/1	12936.10	157101.19	290557.13	1586.30	16172.27	5381.95	5268.00
ES-06-30/2	12567.01	152934.47	263298.03	1297.17	15745.73	5154.19	5200.72
ES-06-30/3	12164.82	150143.52	255495.56	1496.34	17596.75	5987.73	5845.05
ES-06-30/4	12667.17	152734.47	254230.30	1468.28	16012.84	5646.85	5609.01
Mean	12583.78	153228.41	265895.26	1462.02	16381.90	5542.68	5480.70
STD	319.84	2877.81	16923.14	120.88	828.80	358.55	301.58
% Deviation	2.54	1.88	6.36	8.27	5.06	6.47	5.50
ES-06-23/1	7400.34	95527.91	189659.03	682.86	92605.86	3525.46	3437.25
ES-06-23/2	7247.51	92456.85	168460.44	617.17	89932.41	4052.36	4074.03
ES-06-23/3	7113.84	95967.80	166802.53	634.14	91478.30	3640.20	3654.81
ES-06-23/4	7227.36	95121.25	166878.03	689.52	94409.71	3596.72	3596.15
Mean	7247.26	94768.45	172950.01	655.92	92106.57	3703.69	3690.56
STD	117.80	1579.37	11165.54	35.73	1886.39	237.21	271.67
% Deviation	1.63	1.67	6.46	5.45	2.05	6.40	7.36
ES-06-25/1	4980.35	55587.63	125751.36	482.05	170726.45	2654.35	2656.99
ES-06-25/2	5100.51	56718.80	117845.49	479.99	177301.77	2940.40	2917.30
ES-06-25/3	5186.85	56555.03	110993.97	481.89	178160.30	2641.29	2645.43
ES-06-25/4	5237.36	57804.85	113866.17	555.93	178785.11	2652.79	2695.18
Mean	5126.27	56666.58	117114.25	499.97	176243.41	2722.21	2728.73
STD	112.50	908.29	6406.83	37.32	3727.90	145.58	127.50
% Deviation	2.19	1.60	5.47	7.46	2.12	5.35	4.67
ES-06-28/1	7349.94	93127.94	186014.22	556.14	100276.00	3539.52	3515.21
ES-06-28/2	7725.27	99087.50	183856.50	581.07	106054.05	3846.14	3867.79
ES-06-28/3	7812.06	99401.15	176721.59	601.66	106044.44	3985.28	3983.00
ES-06-28/4	7396.50	96384.03	169003.72	625.23	103512.27	3689.66	3611.84
Mean	7570.94	97000.16	178899.01	591.03	103971.69	3765.15	3744.46
STD	231.82	2915.22	7699.80	29.43	2738.72	192.89	217.76
% Deviation	3.06	3.01	4.30	4.98	2.63	5.12	5.82
ES-06-34/1	5866.51	69749.77	179482.97	644.61	118844.45	4620.77	4589.79
ES-06-34/2	6117.13	68174.05	158703.75	650.87	119937.18	3726.64	3802.95
ES-06-34/3	5898.42	70006.38	152947.39	658.57	122061.32	4372.50	4441.67
ES-06-34/4	5646.66	66650.33	144880.55	616.86	121724.13	2969.61	2940.75
Mean	5882.18	68645.13	159003.67	642.73	120641.77	3922.38	3943.79
STD	192.51	1557.17	14783.24	18.17	1518.05	738.57	750.81
% Deviation	3.27	2.27	9.30	2.83	1.26	18.83	19.04
ES-06-37/1	8979.59	115617.84	223012.19	755.80	82298.31	4390.07	4419.43
ES-06-37/2	8622.21	111810.97	205037.05	781.68	79552.56	3917.70	3915.26
ES-06-37/3	8600.80	112344.80	200546.83	725.28	80802.81	4438.52	4422.95
ES-06-37/4	8640.01	112234.62	199434.14	764.00	78679.83	4178.01	4128.61
Mean	8710.65	113002.06	207007.55	756.69	80333.38	4231.08	4221.56
STD	180.01	1758.97	10941.19	23.56	1573.24	237.58	246.42
% Deviation	2.07	1.56	5.29	3.11	1.96	5.62	5.84

Supplementary Table 8, Continued...

Sample name	V	Cr	Mn	Fe	Co	Ni	Cu
ES-06-30/1	158.86	144.35	182.69	45112.40	15.39	60.84	26.40
ES-06-30/2	153.76	138.38	176.76	43964.89	14.62	56.80	159.33
ES-06-30/3	155.68	137.23	172.51	42476.59	14.41	55.18	23.82
ES-06-30/4	155.54	138.59	181.59	44466.43	14.85	57.01	27.30
Mean	155.96	139.64	178.39	44005.08	14.82	57.46	59.21
STD	2.12	3.20	4.69	1122.04	0.42	2.40	66.76
% Deviation	1.36	2.29	2.63	2.55	2.85	4.17	112.75
ES-06-23/1	76.46	80.28	158.59	27638.72	****	27.74	16.44
ES-06-23/2	75.17	82.00	156.97	26700.83	9.51	28.08	15.98
ES-06-23/3	76.75	79.18	151.70	25693.77	9.36	25.21	14.69
ES-06-23/4	77.46	80.28	155.36	26317.78	9.60	26.95	15.59
Mean	76.46	80.44	155.66	26587.78	9.49	27.00	15.68
STD	0.96	1.17	2.95	814.33	0.12	1.28	0.74
% Deviation	1.25	1.45	1.89	3.06	1.28	4.74	4.74
ES-06-25/1	41.61	45.69	203.18	17717.88	12.31	15.23	5.96
ES-06-25/2	43.29	47.11	200.36	17489.39	14.72	15.13	5.66
ES-06-25/3	43.31	46.97	198.17	17396.24	13.04	14.94	5.90
ES-06-25/4	43.42	53.74	197.18	17169.63	26.63	17.38	6.22
Mean	42.91	48.38	199.72	17443.29	16.68	15.67	5.94
STD	0.87	3.63	2.66	227.03	6.71	1.15	0.23
% Deviation	2.02	7.51	1.33	1.30	40.26	7.32	3.88
ES-06-28/1	88.89	79.72	171.80	26748.64	31.50	30.61	23.14
ES-06-28/2	96.14	84.18	175.63	27127.69	12.59	29.05	12.49
ES-06-28/3	99.03	87.85	175.92	27302.00	32.59	31.97	10.55
ES-06-28/4	95.62	84.26	171.33	26610.29	13.61	28.81	32.88
Mean	94.92	84.00	173.67	26947.16	22.57	30.11	19.77
STD	4.29	3.33	2.44	322.18	10.95	1.47	10.35
% Deviation	4.52	3.96	1.41	1.20	48.53	4.90	52.35
ES-06-34/1	60.02	64.70	186.53	21972.23	15.61	21.03	6.75
ES-06-34/2	62.35	63.78	184.96	21528.15	16.09	21.79	7.40
ES-06-34/3	64.57	64.71	182.70	21490.28	16.82	20.87	100.36
ES-06-34/4	61.30	68.92	179.92	20949.36	15.79	22.86	7.30
Mean	62.06	65.53	183.53	21485.01	16.08	21.64	30.45
STD	1.93	2.30	2.87	418.81	0.53	0.91	46.61
% Deviation	3.10	3.52	1.57	1.95	3.32	4.20	153.04
ES-06-37/1	105.73	101.69	199.42	39774.52	23.14	37.86	29.06
ES-06-37/2	100.60	101.30	185.79	37833.68	21.84	37.54	8.95
ES-06-37/3	105.18	101.11	185.77	37999.48	21.45	36.37	19.06
ES-06-37/4	102.35	95.90	184.82	37345.69	21.67	35.70	10.72
Mean	103.47	100.00	188.95	38238.34	22.03	36.87	16.95
STD	2.42	2.74	6.99	1061.05	0.76	1.01	9.20
% Deviation	2.34	2.74	3.70	2.77	3.45	2.73	54.28

Supplementary Table 8, Continued...

Sample name	Zn	As	Sr	Mo	Cd	Sn	Sb
ES-06-30/1	95.66	19.00	253.32	0.49	<0.107	6.66	1.44
ES-06-30/2	90.27	17.62	222.69	0.25	<0.093	6.35	1.09
ES-06-30/3	86.77	21.79	220.22	0.24	0.11	5.97	1.14
ES-06-30/4	91.00	18.60	226.88	0.42	0.10	6.37	1.12
Mean	90.93	19.25	230.78	0.35	0.10	6.34	1.20
STD	3.66	1.79	15.28	0.12	0.01	0.28	0.16
% Deviation	4.02	9.29	6.62	35.46	8.32	4.47	13.78
ES-06-23/1	99.51	13.85	340.61	0.17	0.14	5.02	0.81
ES-06-23/2	99.55	11.14	303.99	0.14	<0.066	4.94	0.69
ES-06-23/3	94.51	10.79	318.48	0.14	0.08	5.06	0.81
ES-06-23/4	97.25	10.46	317.31	0.17	0.10	5.04	0.69
Mean	97.71	11.56	320.10	0.15	0.11	5.02	0.75
STD	2.39	1.55	15.17	0.02	0.03	0.05	0.07
% Deviation	2.44	13.42	4.74	10.19	31.57	1.05	8.99
ES-06-25/1	41.51	5.76	526.39	0.16	0.08	3.26	0.53
ES-06-25/2	44.49	6.24	550.51	0.12	0.09	3.54	0.63
ES-06-25/3	45.39	4.85	561.25	0.14	0.07	3.32	0.56
ES-06-25/4	42.73	5.10	568.98	0.27	0.08	3.42	0.81
Mean	43.53	5.49	551.78	0.17	0.08	3.39	0.63
STD	1.74	0.63	18.55	0.07	0.01	0.12	0.12
% Deviation	4.00	11.51	3.36	37.94	7.23	3.62	19.43
ES-06-28/1	68.87	13.02	440.52	0.15	0.13	4.14	0.80
ES-06-28/2	105.49	14.17	473.83	0.22	0.14	4.56	0.88
ES-06-28/3	75.81	15.14	485.52	0.13	0.09	4.69	0.89
ES-06-28/4	71.63	11.96	480.99	0.11	0.07	4.81	0.80
Mean	80.45	13.57	470.22	0.15	0.11	4.55	0.84
STD	16.94	1.38	20.37	0.04	0.03	0.29	0.05
% Deviation	21.05	10.17	4.33	29.35	32.25	6.41	5.87
ES-06-34/1	47.45	11.86	430.63	0.43	0.16	4.79	0.91
ES-06-34/2	51.81	10.36	419.45	0.52	0.11	4.24	0.78
ES-06-34/3	49.60	9.81	444.63	0.35	0.06	4.05	0.78
ES-06-34/4	51.88	9.02	442.73	0.44	<0.075	3.78	0.69
Mean	50.19	10.26	434.36	0.44	0.11	4.22	0.79
STD	2.11	1.20	11.72	0.07	0.05	0.43	0.09
% Deviation	4.20	11.68	2.70	16.11	45.48	10.14	11.30
ES-06-37/1	98.69	25.28	426.90	0.26	0.14	5.76	1.08
ES-06-37/2	91.16	22.84	448.13	0.23	<0.095	5.69	0.91
ES-06-37/3	111.87	24.24	404.07	0.28	0.13	5.34	0.93
ES-06-37/4	92.65	21.41	494.66	0.19	0.11	5.65	1.00
Mean	98.59	23.44	443.44	0.24	0.13	5.61	0.98
STD	9.43	1.68	38.60	0.04	0.02	0.19	0.08
% Deviation	9.57	7.18	8.70	16.40	13.95	3.31	7.90

Supplementary Table 8, Continued...

Sample name	Ba	Hg	Tl	Th	U	K
ES-06-30/1	719.22	0.13	1.41	17.15	3.12	49594.91
ES-06-30/2	695.31	0.11	1.29	13.25	2.64	47616.35
ES-06-30/3	695.32	0.11	1.32	14.37	3.30	46669.59
ES-06-30/4	708.16	0.17	1.41	13.37	2.61	48053.40
Mean	704.50	0.13	1.36	14.54	2.92	47983.56
STD	11.53	0.03	0.06	1.81	0.35	1219.66
% Deviation	1.64	20.12	4.56	12.48	11.85	2.54
ES-06-23/1	486.36	0.11	0.94	11.25	1.93	28985.05
ES-06-23/2	481.54	0.11	0.91	12.74	2.66	28210.69
ES-06-23/3	506.65	0.11	0.91	11.38	2.28	30102.80
ES-06-23/4	508.08	0.16	0.90	14.29	2.08	29734.74
Mean	495.66	0.12	0.92	12.42	2.24	29258.32
STD	13.67	0.02	0.02	1.42	0.32	839.11
% Deviation	2.76	17.04	2.02	11.44	14.13	2.87
ES-06-25/1	281.75	0.11	0.53	8.24	1.26	17502.81
ES-06-25/2	292.70	0.10	0.53	8.62	2.12	17879.75
ES-06-25/3	298.98	0.10	0.54	7.56	1.50	18519.89
ES-06-25/4	302.35	0.10	0.57	12.49	1.66	18483.16
Mean	293.95	0.10	0.54	9.23	1.64	18096.40
STD	9.06	0.01	0.02	2.22	0.36	492.68
% Deviation	3.08	6.42	3.76	24.05	22.18	2.72
ES-06-28/1	433.29	0.10	0.86	9.90	1.65	29614.61
ES-06-28/2	486.74	0.12	0.96	10.31	1.53	31190.39
ES-06-28/3	497.69	0.12	0.99	11.48	1.91	32584.18
ES-06-28/4	482.06	0.11	0.94	11.30	1.91	31660.76
Mean	474.95	0.11	0.94	10.75	1.75	31262.49
STD	28.53	0.01	0.05	0.76	0.19	1241.80
% Deviation	6.01	8.58	5.85	7.11	10.92	3.97
ES-06-34/1	417.04	0.25	0.69	10.46	2.16	21822.58
ES-06-34/2	435.36	0.21	0.66	10.94	2.20	21970.46
ES-06-34/3	480.03	0.24	0.66	8.40	1.83	22537.47
ES-06-34/4	496.24	0.27	0.65	10.91	2.34	21740.76
Mean	457.17	0.24	0.67	10.18	2.13	22017.82
STD	37.13	0.03	0.02	1.21	0.22	359.24
% Deviation	8.12	10.70	2.89	11.84	10.13	1.63
ES-06-37/1	682.44	0.19	1.13	12.32	2.06	37268.27
ES-06-37/2	696.92	0.21	1.13	11.54	1.94	36292.91
ES-06-37/3	640.12	0.17	1.11	14.78	4.29	37354.25
ES-06-37/4	778.28	0.18	1.09	12.06	2.05	37163.90
Mean	699.44	0.19	1.12	12.68	2.59	37019.83
STD	57.82	0.02	0.02	1.44	1.14	490.83
% Deviation	8.27	9.71	1.72	11.36	44.02	1.33

Supplementary Table 8, Continued...

Sample name	Mg	Al	Si	P	Ca	Ti47	Ti49
ES-06-38/1	9076.63	90436.35	198276.91	2822.58	114233.27	5717.21	5764.30
ES-06-38/2	8838.42	93287.41	185814.16	3122.59	117231.88	3483.06	3439.29
ES-06-38/3	8365.88	90822.89	177291.81	2797.63	115343.06	4089.86	4062.59
ES-06-38/4	8261.00	86562.54	166615.88	2830.39	113939.01	3429.67	3486.77
Mean	8635.48	90277.30	181999.69	2893.30	115186.81	4179.95	4188.24
STD	386.75	2779.88	13395.57	153.50	1491.42	1067.69	1088.23
% Deviation	4.48	3.08	7.36	5.31	1.29	25.54	25.98
ES-06-49/1	8221.65	108674.16	204773.75	564.42	69366.02	4136.80	4112.11
ES-06-49/2	7766.60	106431.51	192295.05	540.34	65716.31	4193.00	4215.93
ES-06-49/3	8396.93	106984.02	191119.03	540.64	66696.92	3685.15	3710.09
ES-06-49/4	7981.86	108718.29	189236.28	541.09	66194.61	4231.03	4162.69
Mean	8091.76	107702.00	194356.03	546.62	66993.47	4061.50	4050.21
STD	275.56	1170.13	7058.48	11.87	1631.59	253.86	230.67
% Deviation	3.41	1.09	3.63	2.17	2.44	6.25	5.70
ES-08-19a/1	8883.27	128420.20	251836.33	1639.72	79378.01	3804.53	3758.27
ES-08-19a/2	9269.89	134342.98	251947.95	1640.03	82623.62	3835.69	3829.00
ES-08-19a/3	8877.91	127567.05	234694.52	1647.30	81161.62	4601.96	4474.20
ES-08-19a/4	8872.12	130708.84	231561.09	1693.41	80834.92	4846.51	4757.96
Mean	8975.80	130259.77	242509.97	1655.12	80999.54	4272.17	4204.86
STD	196.11	3028.15	10908.95	25.77	1331.71	531.61	489.62
% Deviation	2.18	2.32	4.50	1.56	1.64	12.44	11.64
ES-08-46b/1	10458.00	111620.59	214630.13	549.56	79654.90	3425.09	3458.57
ES-08-46b/2	11094.69	115185.93	210286.50	628.94	85355.19	3651.84	3576.41
ES-08-46b/3	10921.68	114386.42	199279.25	663.40	86437.87	3678.24	3691.65
ES-08-46b/4	10682.65	113228.75	192918.53	626.54	83213.12	3425.41	3430.43
Mean	10789.26	113605.42	204278.60	617.11	83665.27	3545.15	3539.27
STD	278.04	1548.05	9954.79	48.08	2990.58	138.86	119.66
% Deviation	2.58	1.36	4.87	7.79	3.57	3.92	3.38
ES-06-36/1	7776.12	81432.14	152402.63	1189.50	110604.74	4049.13	4016.56
ES-06-36/2	7655.31	80009.04	147667.92	1170.28	111626.12	3537.56	3586.25
ES-06-36/3	7510.52	79586.45	141881.98	1127.67	112807.48	4342.38	4299.70
ES-06-36/4	7655.55	79038.17	142465.44	1137.14	112602.70	3583.05	3556.63
Mean	7649.38	80016.45	146104.49	1156.15	111910.26	3878.03	3864.79
STD	108.66	1024.07	4939.07	28.78	1011.53	386.36	358.11
% Deviation	1.42	1.28	3.38	2.49	0.90	9.96	9.27
ES-06-44/1	8529.77	118353.65	201171.25	556.10	74474.77	4745.60	4551.21
ES-06-44/2	8111.82	111573.55	169583.09	543.32	74989.88	3885.14	3780.11
ES-06-44/3	8071.27	111805.20	167072.97	499.60	76628.20	3488.67	3469.12
ES-06-44/4	8296.79	111388.09	160712.63	557.29	77196.00	3783.48	3783.82
Mean	8252.41	113280.12	174634.99	539.08	75822.21	3975.72	3896.07
STD	209.34	3386.65	18080.48	27.07	1296.83	540.09	460.99
% Deviation	2.54	2.99	10.35	5.02	1.71	13.58	11.83

Supplementary Table 8, Continued...

Sample name	V	Cr	Mn	Fe	Co	Ni	Cu
ES-06-38/1	83.46	80.56	226.45	34097.41	11.84	31.01	10.36
ES-06-38/2	84.48	80.48	213.12	31943.58	11.37	29.35	11.38
ES-06-38/3	81.28	77.52	203.00	30830.06	10.65	27.56	11.16
ES-06-38/4	80.74	76.68	197.01	30403.25	10.66	27.24	10.61
Mean	82.49	78.81	209.90	31818.58	11.13	28.79	10.88
STD	1.77	2.00	12.88	1652.17	0.58	1.75	0.47
% Deviation	2.15	2.54	6.14	5.19	5.22	6.07	4.35
ES-06-49/1	95.43	92.61	173.49	33317.87	17.13	32.62	19.42
ES-06-49/2	90.92	89.07	162.00	31421.26	16.04	30.29	9.18
ES-06-49/3	95.17	92.69	177.42	33064.78	17.18	33.23	8.57
ES-06-49/4	95.28	95.16	165.29	31581.36	16.60	31.84	9.94
Mean	94.20	92.38	169.55	32346.32	16.74	32.00	11.78
STD	2.19	2.51	7.13	983.36	0.53	1.27	5.13
% Deviation	2.32	2.71	4.21	3.04	3.19	3.97	43.52
ES-08-19a/1	107.87	109.67	188.21	33682.45	12.99	42.00	22.22
ES-08-19a/2	114.95	113.47	194.04	33745.09	13.49	42.45	21.96
ES-08-19a/3	111.43	110.83	191.12	33534.71	12.94	41.52	21.55
ES-08-19a/4	111.94	110.12	189.50	33410.80	12.85	40.90	21.51
Mean	111.55	111.02	190.72	33593.26	13.07	41.72	21.81
STD	2.90	1.70	2.51	150.25	0.29	0.66	0.34
% Deviation	2.60	1.53	1.32	0.45	2.20	1.59	1.56
ES-08-46b/1	91.61	97.46	208.54	40640.79	15.74	36.26	13.64
ES-08-46b/2	100.01	102.08	215.12	43553.86	14.16	37.34	14.84
ES-08-46b/3	97.89	100.11	205.64	41617.29	13.31	36.83	12.13
ES-08-46b/4	98.25	102.38	203.04	40694.07	13.55	37.01	15.12
Mean	96.94	100.51	208.09	41626.50	14.19	36.86	13.93
STD	3.67	2.27	5.20	1360.86	1.09	0.45	1.36
% Deviation	3.79	2.26	2.50	3.27	7.71	1.23	9.78
ES-06-36/1	79.39	82.27	227.95	28645.87	22.89	24.86	12.74
ES-06-36/2	79.30	77.38	217.76	28503.75	20.80	24.43	10.85
ES-06-36/3	80.08	81.77	220.46	28533.81	20.61	25.27	10.08
ES-06-36/4	80.11	78.43	222.73	28790.40	21.02	24.05	14.93
Mean	79.72	79.96	222.23	28618.46	21.33	24.65	12.15
STD	0.43	2.42	4.32	129.92	1.05	0.53	2.16
% Deviation	0.55	3.03	1.95	0.45	4.94	2.14	17.81
ES-06-44/1	100.99	100.85	196.82	38851.70	10.00	34.66	20.16
ES-06-44/2	97.12	96.84	183.64	37806.53	9.56	33.17	13.82
ES-06-44/3	102.41	101.27	185.00	39558.90	9.84	33.04	13.81
ES-06-44/4	105.70	103.44	193.09	39564.10	9.70	33.48	13.14
Mean	101.56	100.60	189.64	38945.31	9.78	33.59	15.23
STD	3.55	2.75	6.35	829.65	0.19	0.74	3.30
% Deviation	3.50	2.74	3.35	2.13	1.93	2.20	21.67

Supplementary Table 8, Continued...

Sample name	Zn	As	Sr	Mo	Cd	Sn	Sb
ES-06-38/1	68.39	14.83	505.04	0.18	0.15	5.14	0.90
ES-06-38/2	71.56	10.95	516.78	0.18	0.05	4.69	0.81
ES-06-38/3	69.06	13.14	479.90	0.16	0.06	5.06	0.86
ES-06-38/4	65.34	12.46	508.32	0.17	0.10	4.34	0.92
Mean	68.59	12.85	502.51	0.17	0.09	4.81	0.87
STD	2.56	1.61	15.86	0.01	0.04	0.37	0.05
% Deviation	3.73	12.53	3.16	6.75	48.99	7.66	5.71
ES-06-49/1	91.69	16.61	347.12	0.23	0.12	5.62	0.77
ES-06-49/2	80.19	15.21	295.14	0.19	<0.065	5.09	0.85
ES-06-49/3	85.93	15.25	323.07	0.19	0.11	5.43	0.77
ES-06-49/4	78.00	13.88	313.29	0.19	<0.069	5.46	0.84
Mean	83.95	15.24	319.66	0.20	0.12	5.40	0.81
STD	6.15	1.11	21.66	0.02	0.00	0.22	0.04
% Deviation	7.32	7.32	6.78	11.33	3.63	4.13	5.01
ES-08-19a/1	90.31	20.26	299.45	0.15	0.10	5.41	0.73
ES-08-19a/2	95.73	18.30	281.75	0.10	0.14	5.81	0.75
ES-08-19a/3	94.06	17.14	280.94	0.25	0.10	6.62	0.71
ES-08-19a/4	96.38	19.22	239.70	0.11	0.12	5.88	0.80
Mean	94.12	18.73	275.46	0.15	0.12	5.93	0.75
STD	2.72	1.33	25.32	0.07	0.02	0.50	0.04
% Deviation	2.89	7.09	9.19	44.99	18.82	8.51	5.54
ES-08-46b/1	88.44	9.77	500.66	0.22	0.06	4.89	0.87
ES-08-46b/2	104.07	11.94	527.93	0.20	<0.057	5.05	0.99
ES-08-46b/3	104.42	11.55	551.27	0.18	0.06	5.21	1.01
ES-08-46b/4	95.50	10.61	535.35	0.25	<0.086	5.21	0.95
Mean	98.11	10.97	528.80	0.21	0.06	5.09	0.95
STD	7.65	0.97	21.14	0.03	0.00	0.15	0.06
% Deviation	7.80	8.88	4.00	13.80	1.23	3.01	6.60
ES-06-36/1	71.16	15.27	495.13	0.42	0.11	4.47	0.90
ES-06-36/2	72.83	14.58	516.08	0.28	0.17	4.65	0.92
ES-06-36/3	68.07	13.82	514.74	0.34	0.12	4.63	0.85
ES-06-36/4	67.41	13.99	528.30	0.28	0.17	4.78	0.91
Mean	69.87	14.42	513.56	0.33	0.14	4.63	0.90
STD	2.56	0.66	13.72	0.07	0.03	0.13	0.03
% Deviation	3.67	4.55	2.67	19.71	21.77	2.74	3.47
ES-06-44/1	118.78	11.36	384.42	0.20	0.16	5.55	0.95
ES-06-44/2	113.13	11.85	396.60	0.18	0.14	5.39	1.02
ES-06-44/3	103.74	15.13	410.12	0.20	<0.090	5.64	0.93
ES-06-44/4	101.93	12.73	430.56	0.27	0.13	5.85	0.98
Mean	109.40	12.77	405.43	0.21	0.14	5.61	0.97
STD	7.95	1.67	19.77	0.04	0.02	0.19	0.04
% Deviation	7.27	13.11	4.88	17.85	12.51	3.42	4.04

Supplementary Table 8, Continued...

Sample name	Ba	Hg	Tl	Th	U	K
ES-06-38/1	410.84	0.15	0.94	11.01	3.15	29998.82
ES-06-38/2	442.58	0.16	0.92	11.88	3.08	31738.29
ES-06-38/3	442.86	0.14	0.88	12.23	2.61	30317.79
ES-06-38/4	429.55	0.17	0.86	9.15	2.69	29701.14
Mean	431.46	0.15	0.90	11.07	2.88	30439.01
STD	15.08	0.01	0.04	1.38	0.27	902.04
% Deviation	3.50	8.10	4.06	12.45	9.43	2.96
ES-06-49/1	505.78	0.14	1.04	10.99	1.79	33762.95
ES-06-49/2	490.69	0.16	0.98	11.30	2.25	32336.67
ES-06-49/3	518.72	0.15	1.02	13.98	3.14	33053.13
ES-06-49/4	522.05	0.15	1.07	12.04	3.09	34192.70
Mean	509.31	0.15	1.03	12.08	2.57	33336.36
STD	14.26	0.01	0.04	1.34	0.66	815.45
% Deviation	2.80	6.80	3.67	11.12	25.70	2.45
ES-08-19a/1	593.11	0.06	1.20	12.12	2.45	39826.16
ES-08-19a/2	636.61	0.10	1.21	11.63	2.13	55920.05
ES-08-19a/3	606.76	0.12	1.20	12.52	2.50	40915.91
ES-08-19a/4	643.03	0.09	1.23	14.03	2.29	40906.42
Mean	619.88	0.09	1.21	12.58	2.34	44392.14
STD	23.84	0.02	0.01	1.04	0.17	7702.28
% Deviation	3.85	25.59	1.17	8.24	7.15	17.35
ES-08-46b/1	473.18	0.08	1.07	10.67	1.87	35143.31
ES-08-46b/2	530.99	0.08	1.15	11.08	2.22	38046.51
ES-08-46b/3	516.48	0.10	1.17	11.91	2.27	37277.54
ES-08-46b/4	525.81	0.11	1.15	11.16	2.13	38018.07
Mean	511.62	0.09	1.14	11.21	2.12	37121.36
STD	26.32	0.02	0.04	0.52	0.18	1365.90
% Deviation	5.14	16.58	3.91	4.61	8.39	3.68
ES-06-36/1	476.89	0.25	0.86	10.65	1.98	21948.46
ES-06-36/2	487.30	0.29	0.83	11.06	2.36	22022.89
ES-06-36/3	473.96	0.27	0.83	11.61	2.22	22143.56
ES-06-36/4	484.78	0.28	0.89	10.81	2.01	22672.38
Mean	480.73	0.27	0.85	11.03	2.14	22196.82
STD	6.33	0.02	0.03	0.42	0.18	327.07
% Deviation	1.32	6.11	3.32	3.81	8.40	1.47
ES-06-44/1	550.05	0.13	1.14	11.11	1.92	31727.88
ES-06-44/2	571.19	0.12	1.10	12.33	1.81	29075.83
ES-06-44/3	567.43	0.11	1.16	14.28	1.86	31028.63
ES-06-44/4	607.98	0.13	1.25	16.57	2.02	32288.88
Mean	574.16	0.12	1.16	13.57	1.90	31030.31
STD	24.35	0.01	0.06	2.39	0.09	1401.26
% Deviation	4.24	9.62	5.32	17.59	4.75	4.52

Supplementary Table 8, Continued...

Sample name	Mg	Al	Si	P	Ca	Ti47	Ti49
ES-06-22/1	7480.62	93579.34	173982.36	635.25	115984.82	3834.95	3853.07
ES-06-22/2	7211.23	92140.94	160216.59	558.83	114981.97	3440.65	3390.09
ES-06-22/3	7079.27	88610.31	148504.89	775.37	114802.44	3628.55	3640.59
ES-06-22/4	6442.59	84037.34	132302.94	449.38	112522.64	3346.66	3362.12
Mean	7053.43	89591.98	153751.70	604.71	114572.97	3562.70	3561.47
STD	440.15	4251.04	17688.53	136.98	1462.54	216.04	231.23
% Deviation	6.24	4.74	11.50	22.65	1.28	6.06	6.49
ES-06-26/1	4908.32	60542.73	121912.70	393.16	131014.45	3224.08	3264.75
ES-06-26/2	4899.09	58215.53	99218.13	394.64	132942.98	2619.53	2592.20
ES-06-26/3	4922.28	59479.11	99021.45	389.14	133372.55	2887.50	2924.45
ES-06-26/4	4856.61	59008.09	94243.72	416.44	130316.83	3014.61	3015.00
Mean	4896.58	59311.37	103599.00	398.35	131911.70	2936.43	2949.10
STD	28.30	972.49	12423.89	12.29	1477.19	252.77	278.07
% Deviation	0.58	1.64	11.99	3.08	1.12	8.61	9.43
ES-06-24/1	4930.00	32608.27	61325.80	445.25	226323.58	1570.47	1587.64
ES-06-24/2	4810.94	30966.44	56438.05	348.13	220478.25	1453.72	1479.36
ES-06-24/3	4812.08	32618.71	58780.97	409.52	218273.64	2132.92	2185.45
ES-06-24/4	4764.50	31716.35	56906.50	384.20	212347.92	1958.09	2024.35
Mean	4829.38	31977.44	58362.83	396.78	219355.85	1778.80	1819.20
STD	70.65	795.71	2219.59	40.97	5776.14	319.70	339.28
% Deviation	1.46	2.49	3.80	10.33	2.63	17.97	18.65
ES-06-43/1	6310.79	72444.77	126685.68	367.51	62177.06	3221.07	3328.33
ES-06-43/2	6822.70	75631.58	126991.42	377.45	63697.75	2551.27	2592.97
ES-06-43/3	6490.45	73038.74	121566.23	337.04	57128.21	2489.65	2458.30
ES-06-43/4	6335.16	72101.16	122118.53	375.60	61900.36	2470.99	2543.93
Mean	6489.78	73304.06	124340.47	364.40	61225.85	2683.25	2730.88
STD	235.78	1599.28	2896.03	18.74	2843.75	360.19	402.17
% Deviation	3.63	2.18	2.33	5.14	4.64	13.42	14.73
ES-06-47/1	8964.28	124993.10	209028.98	513.74	59940.15	4424.32	4553.08
ES-06-47/2	9149.60	120133.42	202508.95	514.05	56727.81	4318.19	4370.50
ES-06-47/3	9413.39	121505.31	204984.67	562.36	58004.12	4102.23	4202.78
ES-06-47/4	8913.67	118593.73	195974.64	505.34	54718.12	4144.54	4124.41
Mean	9110.24	121306.39	203124.31	523.87	57347.55	4247.32	4312.69
STD	226.12	2730.43	5471.82	25.97	2194.74	150.52	190.31
% Deviation	2.48	2.25	2.69	4.96	3.83	3.54	4.41
ES-06-46/1	10101.14	146974.59	228754.70	524.86	46663.21	4367.92	4481.22
ES-06-46/2	9591.60	141236.50	218284.23	516.08	44302.20	4482.96	4606.22
ES-06-46/3	9582.75	139126.47	214829.81	503.94	45816.55	4109.19	4163.40
ES-06-46/4	10157.01	146075.11	226400.19	543.57	48646.96	3978.74	4047.23
Mean	9858.13	143353.17	222067.23	522.11	46357.23	4234.70	4324.52
STD	313.72	3780.16	6587.57	16.68	1812.18	231.41	262.53
% Deviation	3.18	2.64	2.97	3.19	3.91	5.46	6.07

Supplementary Table 8, Continued...

Sample name	V	Cr	Mn	Fe	Co	Ni	Cu
ES-06-22/1	76.65	84.91	218.03	26524.56	11.80	27.49	19.37
ES-06-22/2	79.75	84.25	204.06	26836.15	11.91	26.87	16.57
ES-06-22/3	76.62	79.44	199.60	26502.66	11.77	25.99	16.03
ES-06-22/4	73.79	77.45	192.09	24934.08	11.00	24.30	24.07
Mean	76.70	81.51	203.45	26199.36	11.62	26.16	19.01
STD	2.43	3.64	10.91	857.16	0.42	1.39	3.68
% Deviation	3.17	4.47	5.36	3.27	3.59	5.30	19.34
ES-06-26/1	46.48	56.06	197.12	21154.10	8.81	19.16	8.40
ES-06-26/2	46.64	70.88	184.22	19975.52	9.15	19.93	7.39
ES-06-26/3	47.57	53.47	183.71	20981.12	8.54	17.79	8.10
ES-06-26/4	47.27	53.50	180.54	20871.62	8.22	17.95	8.05
Mean	46.99	58.48	186.40	20745.59	8.68	18.71	7.99
STD	0.52	8.36	7.33	526.39	0.40	1.02	0.43
% Deviation	1.10	14.29	3.93	2.54	4.56	5.45	5.33
ES-06-24/1	26.87	32.85	236.98	13173.06	16.16	10.51	4.21
ES-06-24/2	25.59	29.66	232.48	12452.25	6.71	10.18	8.03
ES-06-24/3	27.65	31.19	233.98	12900.00	6.35	10.16	4.02
ES-06-24/4	27.37	30.76	234.07	12727.24	8.03	9.87	7.30
Mean	26.87	31.12	234.38	12813.14	9.31	10.18	5.89
STD	0.91	1.32	1.88	302.60	4.62	0.26	2.07
% Deviation	3.40	4.26	0.80	2.36	49.63	2.57	35.19
ES-06-43/1	62.41	61.25	156.39	23699.15	10.70	22.96	7.17
ES-06-43/2	63.98	62.26	155.63	25165.88	11.00	24.26	7.18
ES-06-43/3	64.25	60.85	144.89	23328.16	10.64	22.86	38.88
ES-06-43/4	63.60	60.30	151.93	23827.50	10.81	23.44	11.97
Mean	63.56	61.17	152.21	24005.17	10.79	23.38	16.30
STD	0.81	0.83	5.25	802.25	0.16	0.64	15.22
% Deviation	1.28	1.35	3.45	3.34	1.47	2.73	93.39
ES-06-47/1	100.27	100.43	186.60	36119.35	34.08	38.65	22.50
ES-06-47/2	103.12	101.21	174.90	35741.35	33.77	38.61	12.30
ES-06-47/3	102.97	102.35	187.38	37105.05	34.14	38.66	14.09
ES-06-47/4	101.87	95.21	173.19	35426.13	32.51	37.89	11.58
Mean	102.06	99.80	180.52	36097.97	33.63	38.45	15.12
STD	1.32	3.16	7.51	728.75	0.76	0.38	5.03
% Deviation	1.29	3.17	4.16	2.02	2.26	0.98	33.30
ES-06-46/1	121.53	116.87	165.57	39868.25	17.74	44.60	17.45
ES-06-46/2	117.95	111.08	153.80	37956.20	16.64	42.19	15.68
ES-06-46/3	120.11	112.85	154.40	39009.36	17.15	43.56	23.95
ES-06-46/4	124.83	118.98	161.25	39693.73	17.96	44.90	16.61
Mean	121.11	114.95	158.76	39131.89	17.37	43.81	18.42
STD	2.89	3.62	5.66	867.02	0.60	1.22	3.76
% Deviation	2.38	3.15	3.57	2.22	3.43	2.80	20.38

Supplementary Table 8, Continued...

Sample name	Zn	As	Sr	Mo	Cd	Sn	Sb
ES-06-22/1	76.93	9.14	385.32	0.17	0.11	4.71	0.81
ES-06-22/2	81.63	9.38	401.18	0.12	0.12	5.10	0.80
ES-06-22/3	82.05	11.37	417.45	0.14	0.14	5.00	0.82
ES-06-22/4	70.29	8.44	401.43	0.17	0.09	4.78	0.83
Mean	77.73	9.58	401.35	0.15	0.11	4.90	0.82
STD	5.47	1.26	13.12	0.02	0.02	0.18	0.01
% Deviation	7.04	13.11	3.27	15.84	19.20	3.74	1.58
ES-06-26/1	52.22	6.21	446.28	0.27	0.12	5.83	0.75
ES-06-26/2	55.89	6.75	478.64	0.14	0.12	4.04	0.81
ES-06-26/3	56.80	5.81	497.37	0.13	0.10	4.04	0.84
ES-06-26/4	54.39	5.74	488.90	0.15	0.10	4.21	0.90
Mean	54.83	6.13	477.80	0.17	0.11	4.53	0.82
STD	2.00	0.46	22.36	0.07	0.01	0.87	0.06
% Deviation	3.65	7.57	4.68	37.70	12.02	19.21	7.62
ES-06-24/1	78.76	3.66	586.35	0.08	0.18	1.85	0.31
ES-06-24/2	66.49	3.68	590.60	0.07	0.23	1.90	0.31
ES-06-24/3	51.66	4.43	580.98	0.10	0.05	2.12	0.27
ES-06-24/4	67.96	3.25	603.03	0.07	0.13	1.86	0.34
Mean	66.22	3.76	590.24	0.08	0.15	1.93	0.31
STD	11.14	0.49	9.39	0.01	0.07	0.13	0.03
% Deviation	16.82	13.09	1.59	16.46	49.72	6.56	9.88
ES-06-43/1	69.97	9.81	322.71	0.15	0.08	3.19	0.68
ES-06-43/2	74.37	12.26	336.16	0.14	0.06	3.26	0.75
ES-06-43/3	70.34	11.70	310.65	0.15	0.05	3.71	0.73
ES-06-43/4	91.95	10.69	340.04	0.12	0.09	3.25	0.88
Mean	76.66	11.12	327.39	0.14	0.07	3.35	0.76
STD	10.39	1.09	13.40	0.02	0.02	0.24	0.09
% Deviation	13.55	9.77	4.09	11.68	24.68	7.17	11.21
ES-06-47/1	117.83	14.39	322.87	0.18	0.14	5.90	0.91
ES-06-47/2	173.77	17.55	346.16	0.26	0.09	6.05	1.09
ES-06-47/3	130.52	19.37	340.96	0.23	0.11	6.36	1.12
ES-06-47/4	154.75	15.74	332.73	0.26	0.06	6.96	1.06
Mean	144.22	16.76	335.68	0.23	0.10	6.32	1.05
STD	24.95	2.17	10.17	0.04	0.03	0.47	0.09
% Deviation	17.30	12.93	3.03	15.20	33.44	7.43	8.93
ES-06-46/1	125.89	16.72	292.99	0.20	0.10	6.30	1.17
ES-06-46/2	139.06	16.42	307.18	0.19	0.09	6.33	1.20
ES-06-46/3	136.74	16.74	296.39	0.23	0.10	6.50	1.28
ES-06-46/4	133.92	15.42	320.70	0.26	0.10	6.56	1.41
Mean	133.90	16.33	304.32	0.22	0.10	6.42	1.27
STD	5.74	0.62	12.49	0.03	0.01	0.13	0.11
% Deviation	4.29	3.80	4.10	13.38	5.64	1.98	8.48

Supplementary Table 8, Continued...

Sample name	Ba	Hg	Tl	Th	U	K
ES-06-22/1	504.81	0.18	0.94	12.73	2.43	24790.66
ES-06-22/2	546.65	0.20	0.93	10.48	5.00	25647.49
ES-06-22/3	519.87	0.18	0.93	14.76	2.25	25170.99
ES-06-22/4	508.78	0.25	0.84	15.53	2.89	23946.01
Mean	520.03	0.20	0.91	13.38	3.14	24888.79
STD	18.86	0.03	0.05	2.26	1.27	719.66
% Deviation	3.63	15.63	5.03	16.92	40.33	2.89
ES-06-26/1	476.99	0.16	0.59	7.56	1.21	16469.94
ES-06-26/2	377.45	0.12	0.56	6.94	1.35	16637.26
ES-06-26/3	449.67	0.13	0.57	9.43	1.35	17031.71
ES-06-26/4	381.58	0.15	0.55	12.02	2.73	16064.16
Mean	421.42	0.14	0.57	8.99	1.66	16550.77
STD	49.69	0.02	0.02	2.28	0.72	400.88
% Deviation	11.79	13.86	3.03	25.39	43.03	2.42
ES-06-24/1	160.63	0.12	0.33	5.85	1.05	10754.10
ES-06-24/2	155.33	0.13	0.33	5.86	1.07	7065.88
ES-06-24/3	169.87	0.12	0.33	5.14	1.18	7571.96
ES-06-24/4	166.98	0.12	0.32	5.21	1.15	11195.39
Mean	163.20	0.12	0.33	5.52	1.11	9146.83
STD	6.51	0.00	0.00	0.39	0.06	2128.42
% Deviation	3.99	1.94	1.51	7.14	5.61	23.27
ES-06-43/1	270.64	0.11	0.67	8.14	1.23	15581.92
ES-06-43/2	290.27	0.13	0.77	8.92	1.18	15906.37
ES-06-43/3	287.33	0.11	0.72	8.39	1.49	15862.77
ES-06-43/4	293.56	0.10	0.72	11.16	1.32	15761.71
Mean	285.45	0.11	0.72	9.15	1.31	15778.19
STD	10.20	0.01	0.04	1.38	0.14	144.20
% Deviation	3.57	11.49	5.61	15.05	10.38	0.91
ES-06-47/1	586.34	0.17	1.16	14.14	4.43	32219.32
ES-06-47/2	534.16	0.19	1.20	14.26	2.72	26754.69
ES-06-47/3	530.87	0.19	1.20	14.69	2.97	27629.15
ES-06-47/4	536.83	0.17	1.23	14.50	2.98	27405.71
Mean	547.05	0.18	1.20	14.40	3.28	28502.22
STD	26.31	0.01	0.03	0.25	0.78	2505.68
% Deviation	4.81	8.18	2.40	1.71	23.80	8.79
ES-06-46/1	781.70	0.11	1.40	14.77	2.31	47815.57
ES-06-46/2	555.02	0.11	1.35	14.44	2.39	37421.98
ES-06-46/3	552.22	0.13	1.43	14.45	2.30	32921.27
ES-06-46/4	583.99	0.11	1.48	16.50	2.49	34701.71
Mean	618.23	0.11	1.42	15.04	2.37	38215.13
STD	109.92	0.01	0.05	0.99	0.09	6662.50
% Deviation	17.78	9.69	3.85	6.55	3.71	17.43

Supplementary Table 8, Continued...

Sample name	All concentrations in ppm						
	Mg	Al	Si	P	Ca	Ti47	Ti49
ES-06-45/1	8979.60	147945.16	208830.36	527.45	69167.96	4017.61	4122.48
ES-06-45/2	9078.37	130127.06	205367.03	474.71	64588.29	3971.70	4052.03
ES-06-45/3	9351.34	130116.98	207625.27	570.57	67287.72	4382.24	4457.59
ES-06-45/4	9027.45	124247.70	193114.53	504.65	66916.41	4712.94	4733.73
Mean	9109.19	133109.23	203734.30	519.35	66990.10	4271.12	4341.46
STD	166.39	10270.97	7223.91	40.41	1880.23	347.12	315.74
% Deviation	1.83	7.72	3.55	7.78	2.81	8.13	7.27

Sample name	V	Cr	Mn	Fe	Co	Ni	Cu
ES-06-45/1	102.94	106.32	194.85	41774.44	11.98	41.38	15.22
ES-06-45/2	102.58	100.88	188.84	40466.43	11.85	40.43	13.72
ES-06-45/3	104.90	104.76	197.48	42122.96	12.13	42.65	13.52
ES-06-45/4	103.14	99.63	192.46	39661.87	11.52	39.31	14.75
Mean	103.39	102.90	193.41	41006.43	11.87	40.94	14.30
STD	1.03	3.16	3.67	1145.41	0.26	1.42	0.82
% Deviation	1.00	3.07	1.90	2.79	2.19	3.46	5.70

Sample name	Zn	As	Sr	Mo	Cd	Sn	Sb
ES-06-45/1	98.76	11.90	330.18	0.39	0.09	5.67	1.23
ES-06-45/2	124.93	13.96	329.41	0.30	0.09	5.68	1.15
ES-06-45/3	128.22	12.36	349.08	0.29	0.10	5.86	1.30
ES-06-45/4	125.11	12.27	345.97	0.27	0.10	5.85	1.19
Mean	119.26	12.62	338.66	0.31	0.09	5.77	1.22
STD	13.75	0.91	10.32	0.05	0.01	0.10	0.06
% Deviation	11.53	7.24	3.05	15.94	5.54	1.81	5.25

Sample name	Ba	Hg	Tl	Th	U	K
ES-06-45/1	792.67	0.08	1.13	12.03	2.01	49405.81
ES-06-45/2	483.88	0.07	1.23	12.20	2.16	31210.12
ES-06-45/3	551.83	0.09	1.28	17.49	2.35	37036.91
ES-06-45/4	509.08	0.10	1.27	13.87	2.51	37512.48
Mean	584.37	0.08	1.23	13.90	2.26	38791.33
STD	141.67	0.01	0.07	2.53	0.22	7634.47
% Deviation	24.24	14.97	5.58	18.24	9.67	19.68

Supplementary Table 9, Total inorganic carbon (TIC, weight %), total organic carbon (TOC), stable carbon isotope values ($\delta^{13}\text{C}_{\text{org}}$) at the Madotz section

Thickness measured from the base (m)	Sample	TIC weight %	TOC weight %	$\delta^{13}\text{C}_{\text{org}}$
0	ES.06.03	6.32	0.22	-23.52
3	ES.06.01	0.00	0.20	-23.18
26.56	ES.08.18a	52.29	1.04	-26.21
26.86	ES.08.18b	76.76	0.00	-26.50
27.14	ES.08.18c	31.53	0.22	-25.54
27.41	ES.08.19	71.13	0.08	-26.04
27.56	ES.08.19a	16.89	0.31	-24.34
27.86	ES.08.19c	24.31	0.16	-24.47
28.11	ES.08.19d	32.02	0.14	-24.70
28.81	ES.08.20a	61.75	0.22	-23.09
28.81	ES.08.20aa	64.62	0.14	-23.22
29.06	ES.08.20b	50.06	1.35	-24.39
29.21	ES.06.21	20.33	0.44	-23.64
29.54	ES.06.22	27.12	0.26	-23.60
29.9	ES.06.23	20.02	0.80	-23.31
30.1	ES.06.24	66.19	0.24	-23.08
30.45	ES.06.26	33.73	0.38	-22.29
30.65	ES.06.25	36.99	0.39	-22.07
31.4	ES.06.27	61.84	0.16	-22.55
32.1	ES.06.28	21.73	0.41	-22.55
32.76	ES.06.30	14.09	0.48	-23.13
33.03	ES.06.31	63.44	0.12	-22.59
33.18	ES.06.32	24.74	0.44	-23.03
33.33	ES.06.33	56.31	0.04	-22.22
33.42	ES.06.34	25.41	0.16	-22.55
33.57	ES.06.35	47.33	0.23	-22.41
33.91	ES.06.36	21.12	0.31	-23.60
34.34	ES.06.37	16.52	0.39	-22.23
34.86	ES.06.38	24.35	0.19	-22.80
34.94	ES.06.39	15.80	0.24	-22.72
35.29	ES.06.40	54.42	0.12	-22.74
35.64	ES.06.41	13.43	0.52	-22.59
35.88	ES.06.42	64.68	0.80	-23.47
36.08	ES.06.43	18.94	0.70	-22.38
36.41	ES.06.44	17.03	0.56	-22.24
36.7	ES.06.45	13.36	0.90	-21.96

Supplementary Table 9, Continued...

36.92	ES.06.46	8.16	0.97	-22.37
37.14	ES.06.47	9.12	0.91	-21.84
37.41	ES.06.48	13.06	0.59	-21.73
37.7	ES.06.49	17.28	0.41	-22.21
38.08	ES.06.50	18.30	0.30	-22.52
39.31	ES.06.51	35.61	0.09	-22.47
40.91	ES.06.52	14.02	0.64	-23.95
41.87	ES.06.53	61.82	0.09	-23.33
44.22	ES-08-55	77.60	0.24	-22.85
44.7	ES-08-56	88.42	0.26	-22.81
46.52	ES-08-58	88.22	0.17	-22.09
49.5	ES-08-60	86.40	0.13	-20.61
50	ES-08-61	87.34	0.11	-21.04
50.1	ES-08-61a	87.43	0.17	-21.01
52.49	ES-08-62	89.24	0.16	-20.76
53.79	ES-08-63	93.35	0.13	-20.98

Supplementary Table 10, Total inorganic carbon (TIC, weight %), total organic carbon (TOC), stable carbon isotope values ($\delta^{13}\text{C}_{\text{org}}$) at the Curití section

Thickness measured from the base (m)	Sample	TIC weight %	TOC weight %	$\delta^{13}\text{C}_{\text{org}}$
0.2	CO.09.1A	88.57	0.48	-24.5
0.4	CO.09.1B	67.17	0.41	-23.29
0.5	CO.09.2A	85.21	0.63	-23.46
0.65	CO.09.2B	91.01	0.52	-23.51
0.8	CO.09.2C	93.77	0.05	-24.71
0.93	CO.09.3	31.09	1.43	-22.4
1.1	CO.09.4	81.30	0.67	-22.47
1.25	CO.09.5	61.37	0.54	-21.87
1.35	CO.09.06 lower	77.69	0.73	-23.09
1.5	CO.09.6B upper	64.57	0.17	-22.58
1.6	CO.09.7	0.09	3.59	-22.08
1.7	CO.09.8	84.76	2.63	
1.75	CO.09.9A	15.16	3.28	-21.67
1.85	CO.09.9B	50.53	3.36	-21.58
1.95	CO.09.9C	9.58	4.78	-20.82
2.1	CO.09.10	83.13	2.45	-21.01
2.36	CO.09.11A	5.53	5.16	-21.19
2.55	CO.09.11B	18.43	4.27	-21.62
2.65	CO.09.11C	21.32	3.22	-21.51
2.75	CO.09.11D	41.60	2.26	-21.48
2.85	CO.09.11E	38.42	2.41	-21.61
2.88	CO.09.12	72.83	1.33	-22
2.98	CO.09.13A	31.07	2.94	-21.28
3.1	CO.09.13B	74.61	1.54	-21.83
3.2	CO.09.13C	41.54	3.00	-21.71
3.35	CO.09.14 conc	97.25	0.17	-24.06
3.35	CO.09.14	37.43	3.20	-21.54
3.45	CO.09.15A	10.38	5.10	-21.44
3.55	CO.09.15B	76.27	1.32	-21.66
3.65	CO.09.15C	78.73	1.17	-21.77
3.75	CO.09.15D	34.01	3.35	-21.63
3.85	CO.09.16	24.05	5.24	-21.43
3.92	CO.09.17A1	24.43	4.27	-21.46
4.12	CO.09.17A2	26.35	4.79	-21.35

Supplementary Table 10, Continued...

4.24	CO.09.17A3	19.04	4.43	-21.26
4.45	CO.09.17B*	69.53	3.92	-22.02
4.57	CO.09.17C	33.69	2.99	-21.63
4.6	CO.09.17C*	26.40	7.05	-22.05
4.62	CO.09.17C+5cm	26.40	8.84	-23.56
4.7	CO.09.17D*	38.53	8.19	-21.72
4.7	CO.09.17D	40.68	4.31	-21.61
4.85	CO.09.17D-2*	33.26	7.76	
4.89	CO.09.17E*	18.97	6.04	-21.66
5.05	CO.09.17F	28.80	3.75	-21.85
5.17	CO.09.17F*	65.02	3.29	-21.9
5.35	CO.09.17G*	79.99	2.20	-21.66
5.19	CO.09.17G	81.67	0.80	
5.55	CO.09.18	86.37	1.72	-21.78
5.85	CO.09.19	26.80	1.14	-21.12
5.91	CO.09.20 conc	88.81	0.72	-22.9
6.04	CO.09.21A	77.15	0.81	-21.33
6.04	CO.09.21A*	78.02	1.82	-21.63
6.22	CO.09.21B	54.65	0.91	-21.34
6.22	CO.09.21B*	63.03	3.33	-21.71
6.38	CO.09.21C	6.36	4.20	-21.53
6.51	CO.09.21D-5cm	21.09	2.35	-21.33
6.56	CO.09.21D	30.67		-21.33
6.76	CO.09.21E	38.32		-21.18
6.86	CO.09.21F	91.86	0.21	-23.46
6.96	CO.09.21G	21.23	2.36	-21.26
7.15	CO.09.22 shale	66.33	0.56	-20.47
7.15	CO.09.22 conc	92.47	0.77	-22.52
7.34	CO.09.23A	50.69	0.84	-21.39
7.59	CO.09.23B	48.91	0.67	-21.55
7.79	CO.09.23C	32.81	0.75	-21.53
8	CO.09.24	89.33	0.17	-22.18
8.15	CO.09.25B	43.84	0.62	-21.76
8.3	CO.09.26	94.46	0.23	-22.66
8.575	CO.09.28	92.03	0.72	-22.27
8.675	CO.09.29	31.02	0.98	-21.8
8.8	CO.09.30	90.57	0.21	-22.47
9	CO.09.31	0.00	2.94	-21.85
10.25	CO.09.130	50.87	2.42	-22.08

Supplementary Figure 1, m/z 191, tri-, tetra- and pentacyclic terpanes, sample ES-08-46B

Supplementary Figure 2, m/z 177, norhopanes, sample ES-08-46B

Supplementary Figure 3, m/z 205, ES-08-46B

Supplementary Figure 4, m/z 217, steranes, ES-08-46B

Supplementary Figure 5, m/z 218, steranes, ES-08-46B

Supplementary Figure 6, m/z 259, diasteranes, Sample ES-08-46B

Supplementary Figure 7, m/z 128+142+156+170+184, methylnaphthalenes, sample ES-08-46B

Supplementary Figure 8, m/z 178+192+206, phenanthrenes, sample ES-08-46B

Supplementary Figure 9, m/z 231, triaromatic steroids, sample ES-08-46B

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RECENT PUBLICATIONS

Gaona-Narvaez, T., Maurrasse, F., Moreno-Bedmar, J. (2013). *Stable Carbon Isotope Stratigraphy and Ammonite Biochronology at Madotz (Aralar, Spain): Implications for the Timing and Duration of Oxygen Depletion during OAE-1a*. *Cretaceous Research*, 40 (2013), 143-157.

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Gaona-Narvaez, T., Maurrasse, F.J.-M.R., Etayo-Serna, F., Rebenack, C (November, 2010). *Geochemistry and microfacies of Aptian organic-rich beds of Paja Formation at the proximity of the Santander Massif, Eastern Cordillera of Colombia: its relationship to oceanic anoxic global events*. Poster presented at the annual meeting of the Geological Society of America, Denver, Colorado.

Gaona-Narvaez, T., Moreno-Bedmar, J.A., Maurrasse, F.J.-M.R., Company, M. (September, 2010). *Correlation of stable carbon isotope and ammonite biostratigraphy at Madoz (Aralar, Spain): implications for the timing of its oxygen-depleted facies to OAE-1a*. Paper presented at the international conference on Geoevents, Geological Heritage, and the Role of the IGCP, Caravaca de la Cruz, Spain.

Gaona-Narvaez, T., Maurrasse, F. J.-M.R., Moreno-Bedmar, J.A., Company, M., Rebenack, C. (September, 2009). *Ammonite Biostratigraphy at the Madotz section (Basco-Cantabrian Basin, Spain), Implications for the record of Cretaceous Oceanic Anoxic Event 1a (OAE-1a)*. Poster presented at the meeting of the Spanish Society of Paleontology, Ronda, Spain.

Gaona-Narvaez, T., Maurrasse, F. J.-M.R., Moreno-Bedmar, J.A., Company, M., Rebenack, C., Lamolda, M. (June, 2009). *Microfacies and Geochemistry of a Shallow-water Lower Aptian Carbonate Platform Sequence at the Madotz section (Basco-Cantabrian Basin, Spain), its Relation to Cretaceous Anoxic Event 1a (OAE-1a)*. Poster presented at the annual convention of the American Association of Petroleum Geology, Denver, Colorado.