The Posidonia Shale in the Dutch Offshore: An Optical, Electron Optical and Geochemical Study

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Abstract

The Posidonia Shale Fm in the Dutch Central Graben is well known for its high concentration of orgnic matter. The preservation of organic matter previously have been explained by permanent anoxic conditions and restricted water conditions. Recent studies have shown, however, that low energy settings or quiet water conditions and the subsequent suspension settling are not a prerequisite for deposition of muds and shales, but that depositional energy condition are commonly sufficiently high to rework and advect the sediment. In order to effectively determine the lithofacies variability within a succession it is important to make observations of grain-size, determine the origin of individual components, and make microtextural observations of the rock. Therefore, this study uses a combination of optical, electron optical and geochemical analyses of unusually thin (< 20 µm) polished thin sections to show that the Posidonia Shale Fm is deposited by multiple depositional mechanisms in a dynamic fine-grained siliclastic environment. The thin section analyses shows that the Posidonia Shale Fm is characterised by a stacked succession of mud-sized dominated thin beds often characterised by three-fold internal stratigraphy. These thin beds have an erosional base with on top a silt-dominated unit which is either gradually fining upwards or arranged in low angle laminae. The second unit consists of lamina sets of clay and silt dominated layers which are either horizontal or curved and vary from continuous to discontinuous. The uppermost unit, which is predominantly recognised in the upper part of the Posidonia Shale Fm, is homogeneous and clay dominated. Furthermore, the upper part of the Posidonia Shale Fm is characterised by carbonate micro concretions and a high abundance of pyrite. The geochemical analyses show a concomitant negative carbon isotope excursion, increase in TOC concentration and an increasingly heavier sulphur isotope trend in the upper part of the Posidonia Shale Fm. Furthermore, redox and productivity proxies are enriched in this part of the succession. This typical vertical trend in each thin beds suggests that the sediment-water interface was located below the fair-weather wave base, but in relatively shallow water above the storm wave base. Anoxic conditions below the sediment-water interface prevailed in the lower part of the Posidonia Shale Fm and extended to anoxic to sulphidic bottom water conditions in the upper part of the Posidonia Shale Fm. The three-fold internal stratigraphy, however, shows that these conditions were interrupted by short events, possibly by storm induced wave activity, and the subsequent inflow of oxygen-rich surface waters. The Posidonia Shale Fm is, thus, deposited in a dynamic fine-grained siliclastic environment with an alternation of anoxic and short-term oxic conditions

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1. Introduction

Oceanic anoxic events (OAEs) were short-lived (<1 Ma) episodes of organic carbon burial that were characterised by an interbasinal distribution of discrete intervals of black shale formation and/or pronounced carbon isotopic excursions (Leckie et al., 2002). Most OAEs are found in the Aptian-Turonian interval in the mid-Cretaceous. However, in the Early Toarcian (~183 Ma), organic-rich sediments are deposited at various locations worldwide and often characterised by a negative excursion in carbon isotopes. Therefore, these black shales are considered an OAE, the Toarcian-OAE (T-OAE) (Jenkyns, 1988). These organic-rich facies have been recognised in SW Germany (Rohl et al., 2001), Yorkshire (UK), North Sea (Van Adrichem Boogaert and Kouwe, 1993), France (Farrimond et al., 1989; Mailliot et al., 2009; Van Breugel et al., 2006), and, furthermore, but less laterally extensive than those in NW Europe, in the Atlantic domain (Lusitanian Basin) (Hesselbo et al., 2007; Suan et al., 2008a), in the Alpine-Mediterranean domain (Italy, Austria, Switzerland and Greece)(Ebli et al., 1998; Jenkyns, 1988), and in other localities outside the European and Tethyan domains (Alaska, Canada, Japan, Australia and Argentina) (Jenkyns, 1988 and references therein). The thickness of T-OAE facies is generally in the range of 5-30 m and the more organic-rich sediments are dark, millimeter-laminated, benthos-poor and contain carbonate and pyritic concretions(Jenkyns, 1985). In the Netherlands and Germany, these organic-rich black sediments are known as the Posidonia Shale Fm.

The stable carbon isotope record of the T-OAE is commonly associated with a negative carbon isotope excursion and has been recorded in both organic matter and carbonates. However, this shift seems to be restricted to organic-rich sequences only. Research on the causes and mechanisms behind the T-OAE has been conducted in three regions in Europe, the Early Jurassic epicontinental seas of SW Germany (Rohl et al., 2001; Schmid-Röhl et al., 2002) and Yorkshire (Cohen et al., 2004; McArthur et al., 2000; Sælen et al., 2000), at the northern continental margin of the Tethys in Italy and southern alps (Ebli et al., 1998; Farrimond et al., 1989), and in the Lusitanian Basin (Hesselbo et al., 2007; Suan et al., 2010; Suan et al., 2008a; Suan et al., 2008b). Although no consensus has been reached yet, the debate focusses on two explanations. The first explanation requires a local driver for the carbon isotope excursion, because the negative carbon isotope excursion has been attributed to the recycling of remineralised carbon from the lower levels of an intermittently stratified water column into the photic zone and its subsequent incorporation in photosynthetic phytoplankton (Küspert, 1982; Rohl et al., 2001; Sælen et al., 2000; Schmid-Röhl et al., 2002; Schouten et al., 2000; Van de Schootbrugge et al., 2005). The second explanation suggests that the negative carbon isotope excursion resulted from the rapid release to the ocean and atmosphere of methane from methane hydrate in sediments (Hesselbo et al., 2000). In this explanation methane is a global driver for the carbon isotope excursion.

Research on fine-grained sediments, using field, optical, electron optical, and geochemical methods, revealed previously unavailable information (Macquaker and Gawthorpe, 1993; Macquaker and Howell, 1999; Macquaker et al., 2007; O'Brien and Slatt, 1990; Schieber, 2003; Williams et al., 2001). Schieber (2003) suggested that no geochemical studies of black shales should be conducted without careful sedimentological evaluation because subtle sedimentary features may have a direct bearing on the applicability of proposed genetic models. In addition, recent flume experiments with muddy suspensions have demonstrated that low-energy settings are not a prerequisite for the accumulation of muds and shales (Schieber and Yawar, 2009).This research led to the

understanding that sediment dispersal in mud-dominated successions cannot routinely be attributed to low-energy suspension settling. It appears that seafloor energy levels were commonly sufficiently high to rework and transport advectively the sediment, even in mud-dominated successions that have previously been interpreted as being products of low energy or quiet water deposition (Macquaker et al., 2010; Schieber, 2003; Schieber and Yawar, 2009).

Most studies on the Toarcian black shales focussed on techniques like geochemical analyses and/or isotope analyses (Brumsack, 1991; Farrimond et al., 1989; Jenkyns, 1985; McArthur et al., 2008; McArthur et al., 2000; Pearce et al., 2008; Sælen et al., 2000; Schouten et al., 2000; Van de Schootbrugge et al., 2005), paleontological methods (Mailliot et al., 2009; Suan et al., 2010; Suan et al., 2008a; Van de Schootbrugge et al., 2005), and optical/electron optical analyses (O'Brien, 1990; Pye and Krinsley, 1986). MacQuacker (2007)pointed out that to effectively determine lithofacies variability within siliclastic mudstone successions it is essential to combine field, optical, electron optical and geochemical methods to make direct observations of grain-size, determine the origin of individual components, and make microtextural observations of the rock. However, so far there is only one study performed using the combination of these techniques for the Toarcian black shales (Rohl et al., 2001).

This thesis presents a study of cored sections of the Posidonia Shale Fm of two wells in the Dutch Central Graben, which has been previously interpreted as pelagic deposits under anoxic conditions during a period of high sea-level and basin-floor restriction (Van Adrichem Boogaert and Kouwe, 1993). The aim of this study is to show that shales are not homogeneous successions of mud-dominated sediments, but rather are deposited by multiple depositional mechanisms in a dynamic fine-grained siliclastic environment. By utilising optical, electron optical and geochemical analyses of unusually thin (<20 μm) polished thin sections it is possible to enhance the understanding of these fundamental controls that form the basis for the lithofacies variability within the Posidonia Shale Fm in the Dutch Central Graben.

2. Geological and stratigraphic setting

At the start of the Mesozoic Era, all major present-day landmasses were part of the supercontinent of Pangaea (Stanley, 2005). The break-up of Pangaea commenced in the Triassic with intensified tectonic activity in the Arctic–North Atlantic and between Greenland and Scandinavia and propagated southwards to form the Central Atlantic Ocean during the Middle Jurassic (De Jager, 2007). During the Early Triassic an eastern branch of this rift system propagated southwards leading to the development of the NW European basin and graben system which, in the Middle Triassic, had reached the southern North Sea (Ziegler, 1988; Ziegler, 1990). This east-west tensional regime dominated basin development in the North Sea area from the Late Palaeozoic until the North Atlantic reached its modern physiography during the Eocene and can be related to the development of Jurassic strata in mainly fault-bounded basins (Glennie, 1990; Ziegler, 1988; Ziegler, 1990). Concomitantly, the seafloor spreading centre which formed the Tethys Seaway became more active and propagated westwards which resulted in the re-splitting of Pangaea into Laurasia and Gondwana (Glennie, 1990; Ziegler, 1990).

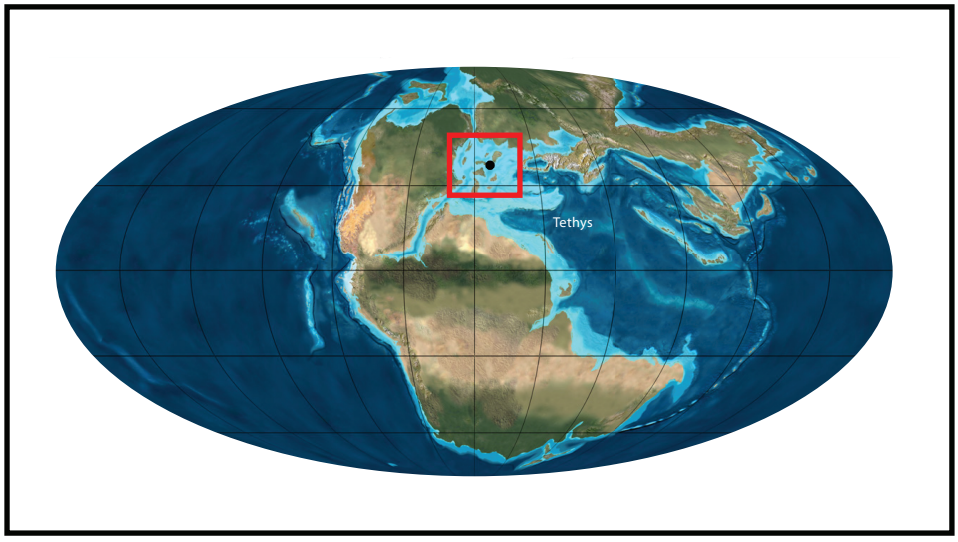

Figure 1
A mollewide projection of the Early Jurassic (~200 Ma). The red square indicates the NW European epi-continental sea. The black dot indicates the location of the Dutch Central Graben. (after Ron Blakey, http:// jan.ucc.nau.edu/~rcb7/)

Between the early Cimmerian (Norian–Rhaetian) and mid–Cimmerian (Aalenian–Callovian/Oxfordian) extensional tectonic phases (Herngreen et al., 2003) there were periods of relative tectonic quiescence in which regional subsidence prevailed and a wide epicontinental sea developed (De Jager, 2007)(figure 1). This resulted in wide, regular facies patterns locally interrupted by halokinesis. This salt movement became first widespread after the Early Triassic and the major salt walls closely follow the boundary faults of the Mesozoic rift basins (De Jager, 2007; Remmelts, 1995; Remmelts, 1996). Within the southern part of this epicontinental sea, which was bounded in the north by the Mid North Sea–Ringkøbing–Fynn High, in the west the Pennine High and in the south by the London–Brabant Massif and Rhenish Massif, two structural elements can be recognised: the Anglo–Dutch Basin and the Dutch Central Graben (figure 2). The latter being the southern extension of the North Sea Central Graben whose N–S trend was already a structural feature from the end-Carboniferous onwards (Geluk, 2007; Glennie, 1990). In the Middle Jurassic, sedimentation was restricted to the rift basins due to the thermal uplift of the Central North Sea Dome of the mid-Cimmerian phase (Underhill and Partington, 1993; Ziegler, 1990). The impact of this uplift is most evident in the northern offshore area of the Netherlands where Lower Jurassic sediments are deeply truncated and formed an unconformity sometimes referred to as “Mid Cimmerian

Unconformity" (Burgers and Mulder, 1991; Van Adrichem Boogaert and Kouwe, 1993) The Central North Sea Dome began to subside again in the Callovian to Oxfordian (Underhill and Partington, 1993; Ziegler, 1990).

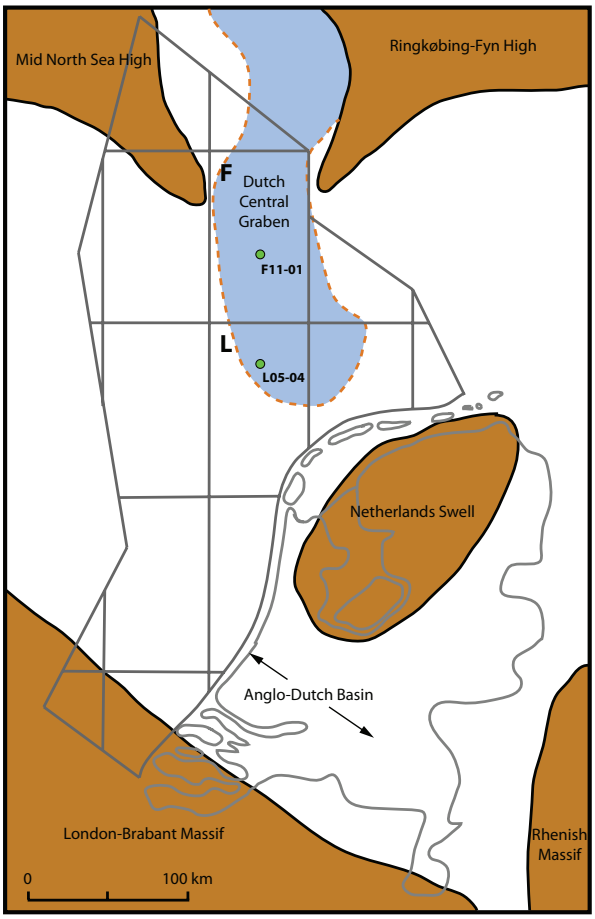

Figure 2
Overview map of the Dutch offshore. In brown the major structural elements, in white the plateau area and in blue the Dutch Central Graben. In the F and L Dutch offshore blocks both the locations of well L05-04 and F11-01 is indicated. (Modified after Van Adrichem Boogaert and Kouwe, 1993; Wong, 2007).

The depositional history of the Late Triassic and Early Jurassic (Rhaetian–Aalenian) started with a basin wide transgression (Rhaetian) followed by the deposition of a very uniform blanket of marine shales in large parts of NW Europe which in the Netherlands are placed in the Altena Group (Herngreen et al., 2003). The basal unit of the Altena Group is the Sleen Fm which consists of marine, fossiliferous, shaly claystones deposited in a shallow, open-marine environment during gentle, uniform subsidence. In the Hettangian to Pliensbachian, a shallow, fairly deep, neritic environment prevailed with the deposition of the Aalburg Fm which consists of a sequence of dark–grey, calcareous, locally silty or sandy claystones locally containing occasional thin argillaceous limestone beds (Van Adrichem Boogaert and Kouwe, 1993). The Early Toarcian is characterised by a period of high sea-level and restricted basin circulation causing anoxic bottom conditions which led to the deposition of dark–grey to brownish–black, bituminous, fissile claystones of the Posidonia Shale Fm and is one of the most important oil source rocks in the southern North Sea area (Herngreen et al., 2003; Van Adrichem Boogaert and Kouwe, 1993; Wong, 2007). Well-oxygenated, open-marine conditions dominated the Late Toarcian and the sediments of the Werkendam Fm were deposited. These sediments comprise grey, slightly marly, shaly claystones with towards the middle a more calcareous, silty to sandy interval. On top of the Werkendam Fm lies the Brabant Fm (Bathonian to Late Callovian age) which was deposited in a shallow and smaller marine basin. The sediments consist of a generally sandy sequence of limestones, marls and claystones, whit increasing sand content towards the top (Van Adrichem Boogaert and Kouwe, 1993).

3. Materials and methods

3.1 Materials

For the present study, we have used core material from the Dutch sector of the North Sea. The material was provided by TNO Built Environment and Geosciences in Utrecht. A total of 51 samples were collected from wells F11-01 and L05-04. Well F11-01 is located at 54.36778˚N and 4.5941668˚E in the centre of the Dutch Central Graben (DCG) and well L05-04 is located at 53.818527˚N and 4.4036946˚E at the southwestern margin of the DCG (figure 2). The samples from well F11-01 are from two cored sections with in between a coring gap. The lower core ranges from 2597 meter below seafloor(mbsf) to 2581 mbsf and has been interpreted as being the Posidonia Shale Fm and the upper core ranges from 2470 mbsf to 2461 mbsf and has been interpreted as the Lower Werkendam Mb. Only the core which contains the Posidonia Shale Fm is presented in this study. The lowermost part of the cored section of well L05-04 has been interpreted as the Aalburg Fm, from 2770–2755 mbsf as the Posidonia Shale Fm and the uppermost part of the cored section as the Rifgronden Mb[1]. Between the Posidonia Shale Fm and the Rifgronden Mb an unconformity is recognised (Abbink, 1998). Fifteen samples of well F11-01, with a sampling resolution of ca. 1 m, and twenty samples of well L05-04, with a sampling resolution that varies from 0.88–2.76 m, are presented in this study (tabel 1). It must be noted, however, that the sampling resolution of both cores is low compared to recent other studies (e.g. McArthur et al., 2008; Rohl et al., 2001). The colour of the samples ranges from dark grey to black in both cores.

Well	Total Number of Samples	Organic Geochemistry#	ICP-MS/OES	Thin Section	SEM/BSE
L05-04	27	20	20	16*	6
F11-01	24	15	15	15*	8

Tabel 1
Overview of number of samples per well and the utilized analyses techniques presented in this study. The four lowermost and three uppermost samples of well L05-04 and the nine sample of the Lower Werkendam Mb of well F11-01 are not presented in this study.
#: Data from Msc. thesis of Abhinav Singh Gill, 2006: Organic geochemical assessment of the Posidonia Shale in the Netherlands.
**: Some thin sections are of poor quality due to the very small size of the rock sample.*

3.2 Methods

The samples were studied on macro scale for sedimentary structures and on micro scale for their texture and fabric. To gain this specific data thin sections are analysed using a flatbed scanner, optical microscope and a SEM (Scanning Electron Microscope) in backscattered electron mode. In addition, all samples are analysed for their inorganic geochemical signature using ICP-MS (Inductively Coupled Plasma - Mass Spectrometry) and ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry).

[1] Netherlands Oil and Gas Portal (http://www.nlog.nl), consulted on april 14, 2010. The site was produced at the request of the Dutch Ministry of Economic Affairs and is being managed by TNO, Geological Survey of the Netherlands.

To make the thin sections suitable for both optical and electron microscopy, the thin sections were prepared, unusually thin, with a thickness of ca. 15 μm. During preparation the sample was impregnated with araldite adhesive before a mm thick slice is cut and glued on a lamina of glass. Subsequently the sample was again impregnated with araldite adhesive for preventing the clay to wash away during polishing. The thin sections were then scanned using a Epson Perfection V700 Photo scanner in 24 bit colour mode with a resolution of 9600 dpi for studying sedimentary structures. For optical petrographic work a Leica DM LB02 optical microscope with attached a Leica DFC 320 digital camera is used. Subsequently the thin sections were coated in carbon and analysed in a Philips XL30–SFEG SEM equipped with a BSE (backscattered electron) detector and EDX analytical system to identify individual minerals. BSE micrographs were obtained operating the microscope at 15 kV and 140 pA, and a working distance between 5–6 mm.

For ICP-MS and ICP-OES analysis a small piece of sample was cut of using a water cooled Diamond Boart rock cutting tool. Subsequently each sample was crushed to rock powder by a, with agate equipped, vibration grinding mill (Herzog, type HSM 100A). Total destruction of 125 mg sample was performed using 2.5 ml mixing acid [HClO4 (72%) : HNO3 (65%) = 3:2] and 2.5 ml HF (48%). The closed vials were put in an aluminium block of 90ºC for 8 hours. Subsequently the open vials were dried in an aluminium block of 160ºC and dissolved in 25 ml HNO3 (4.5%). Finally the closed vials were heated again in an aluminium block of 90ºC for 2 hours. The remaining mixture was analysed using Thermo X-series 2 ICP-MS and a Perkin Elmer Optima 3000 ICP-OES. Analysis of duplicates and standards showed that the relative error was for all elements smaller than 1.5% (2σ). Where needed the results were refined using international standards (ise-921) and Utrecht University in-house standards (SO-1).

4. Results

4.1 Sedimentary aspects

The samples were investigated for sedimentary structures using flatbed scan, optical microscope and SEM micrographs. The general terminology used in this study to describe sedimentary bodies makes a distinction between beds and laminae. A bed is considered a layer of sedimentary rock bounded above and below by bedding surfaces, whereby a bedding surface is produced during periods of nondeposition or abrupt change in depositional conditions. Texture and composition within a bed can vary and a bed can be internally laminated. A lamina is defined as a bed without recognisable internal layering and is relatively uniform in texture and composition (Campbell, 1967).

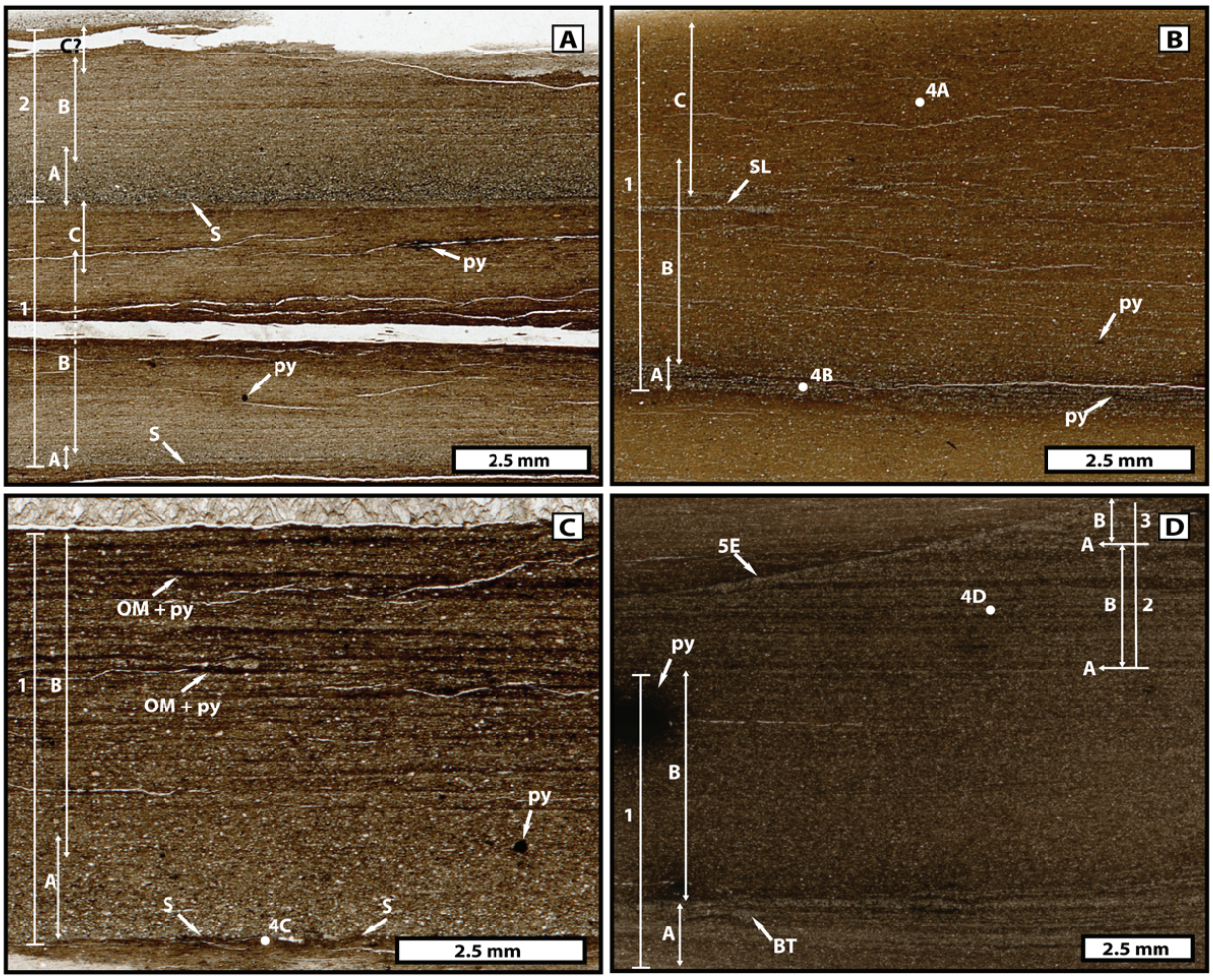

Figure 3
Micrographs of scanned thin sections showing the thin beds (labelled 1–3) and the different units (labelled A–C). A) Thin section 31 (2768.6 mbsf) of well L05-04. B) Thin section 26 (2762.2 mbsf) of well L05-04. C) Thin section 39 (2593.1 mbsf) of well F11-01. D) Thin section 16 (2587.1 mbsf) of well F11-01. In micrographs A and C unit A is silt dominated, fining upwards and gradually changing into unit B which is characterised by laminasets of silt and clay dominated layers. In micrograph C often accentuated by discontinuous layers of organic matter and pyrite. In micrograph A an unit C can be recognised which consists of homogenised clay. In micrographs B and D unit A consists of curved, low angle silt dominated laminae and a sharp contact exists between unit A and B. Unit B is composed of discontinuous, silt and clay dominated layers at the base and grades into a completely homogenised clay unit in micrograph B. In micrograph D unit B consists of a homogenised, fining upwards body which often is overprinted by a diagenetic dolomite lamination. 4A–D and 5E refer to figure 4A–D and figure 5E. Py = pyrite, S = scour features, SL = single discontinuous laminae and BT = bioturbation.

The scanned micrographs (figure 3) show that the majority of the samples is characterised by a stacked succession of mud-sized dominated thin beds. Thickness of the thin beds is not uniform and varies, depending on the sample, between approximately ca. 7 mm and ca. 2 mm. Within the individual thin beds at least two units of different texture and composition can be recognised. The base of each thin bed is erosional and can be recognised by small scale scour relief (labeled "S" in figure 3A and 3C), cross cutting surfaces (labeled "5E" in figure 3D and visible in figure 5E) or abrupt change in grain size (figure 3A–D, and figure 4C). The first unit on top of the erosional base is silt dominated and is either fining upwards or contains curved, low angle laminae (labeled "unit A" in figure 3A–D, and figure 4B). Occasionally, some bioturbation features are visible in this unit (labeled "BT" in figure 3D). This silt dominated unit is followed by a unit which is increasingly upward enriched in clay. This unit can be partially or completely characterised by lamina sets of silt and clay dominated layers which are either horizontal or curved and vary from being continuous to discontinuous (labeled "unit B" in figure 3). The clay dominated lamina sets increase upwards and occasionally grade into a homogeneous clay dominated body which, then, can be identified as a third unit (labeled "unit C" in figure 3, and figure 4A). The overall vertical trend in both wells is that the silt dominated unit decreases in thickness upwards in the cored section, while clay becomes more dominant. Furthermore, the upper part (2587.1 – 2583.1 mbsf) of the cored

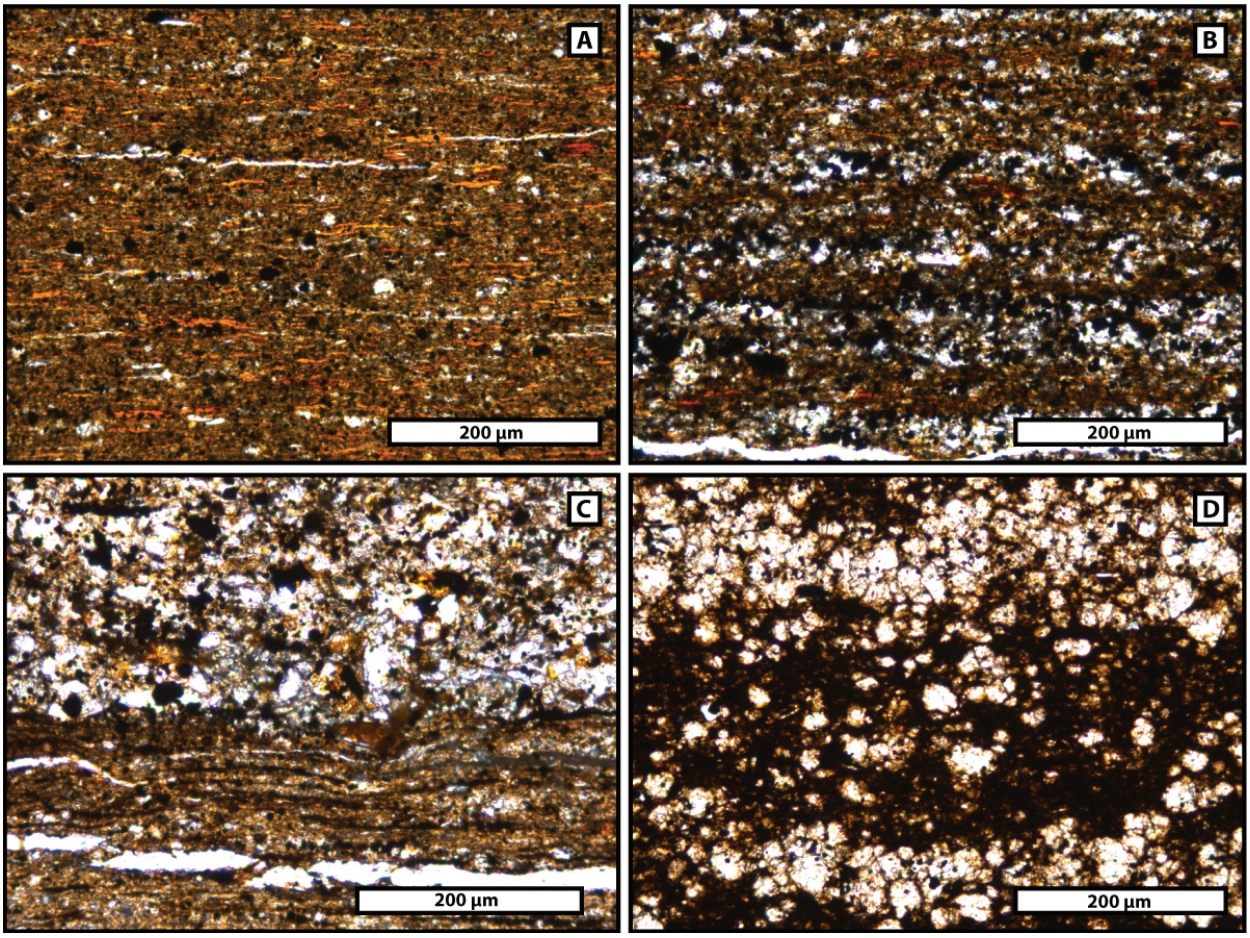

Figure 4
Micrographs. Locations of the images are indicated in figure 3. A) Thin section 26 (2762.2 mbsf) of well L05-04. Image of homogenised clay unit. Very clearly visible are the many algae cysts coloured bright orange. B) Thin section 26 (2762.2 mbsf) of well L05-04. Silt dominated laminae of unit A. C) Thin section 39 (2593.1 mbsf) of well F11-01. Erosion surface between the clay dominated unit (lower part) and the silt dominated unit (upper part). D) Thin section 16 (2587.1 mbsf) of well F11-01. Diagenetic dolomite dominated laminae with a intercalated clay and pyrite lamina. In above images the brownish colours represent clay minerals, the white colours are quart grains (except in D where they represent dolomite crystals), the orange colours are organic matter particles and the black mineral phase is pyrite.

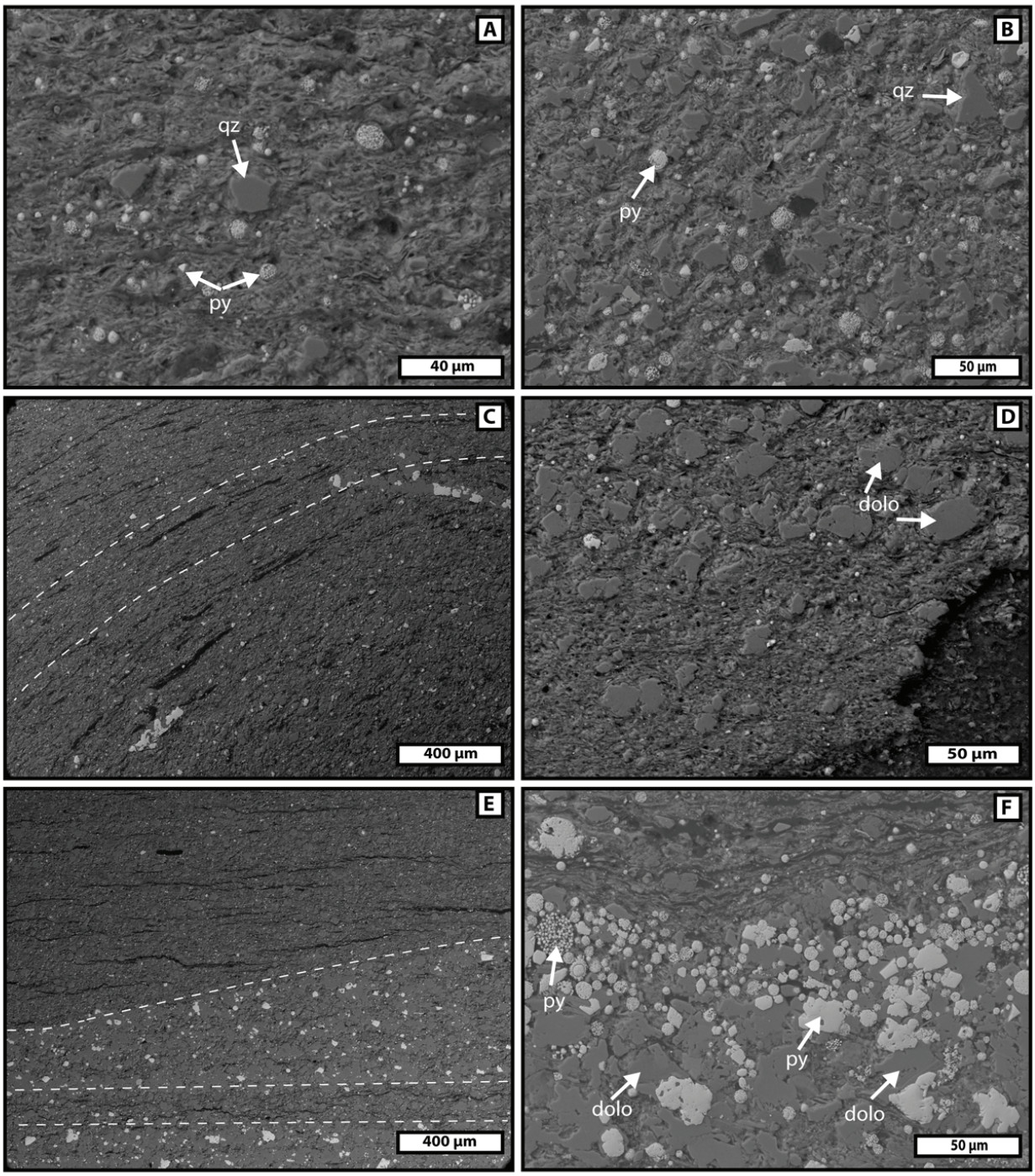

Figure 5

SEM/BSE micrographs. A) Thin section 31 (2768.6 mbsf) of well L05-04. Images of a clay dominated unit. The large grains in the middle are quartz, the white round minerals are pyrite framboids and the black colour is organic matter. B) Thin section 31 (2768.6 mbsf) of well L05-04. Image of silt-sized quartz dominated unit. Again the large grains are quartz, the white minerals are pyrite framboids. The black spots are artefacts of thin section preparation. C) Thin section 27 (2763.1 mbsf) of well L05-04. A close-up of convolute lamination. D) Thin section 27 (2763.1 mbsf) of well L05-04. Detrital dolomite grains. The grains are relatively angular and do not form concatenations. Note the low abundance of pyrite with respect to image F. E) Thin section 16 (2587.1 mbsf) of well F11-01. The position of the image is approximated in figure 3 and represent the erosional surface (inclined dashed line). The horizontal dashed lines divide diagenetic dolomite lamina and clay dominated lamina. F) Thin section 15 (2586.1 mbsf) of well F11-01. Image of diagenetic dolomite lamina and clay dominated lamina. Note the abundant pyrite presence in the dolomite lamina. The pyrite (white coloured minerals) is present as both framboids and euhedral crystals

section of well F11-01 is characterised by the presence of dolomite (figure 5D). These dolomite enrichments cause often horizontal concatenations (figure 5E and 5F) which alternate with the clay dominated laminae (figure 4D) and can, therefore, easily be mistaken for silt-sized quartz laminae. Although the silt content is decreasing upward these dolomite concatenations can give an opposite impression. However, in the localities where physical processes were active, such as the erosional surfaces, quartz grains are found.

On microscale (figure 5) the silt-sized dominated basal unit is primarily composed of quartz grains and pyrite (figure 5B). Pyrite is present either in framboidal form or as larger euhedral crystals in between the single quartz grains. The same texture accounts for the silt dominated laminae in the second unit. The clay dominated laminae of this unit are mainly composed of clay minerals, pyrite and organic matter. The latter is either finely disseminated or present as small recognisable bodies. Pyrite is again present both as framboids and euhedral crystals. Both the framboids and the euhedral crystals are smaller in the clay dominated laminae in respect to the silt dominated laminae. The clay minerals tend to be flocculated in the lower part of the cored sections of both wells, while being laminated in the upper part. The dolomite in the upper part (2587.1 – 2583.1 mbsf) of the cored section of well F11-01 forms often large concatenations in which pyrite tend to be more enriched (figure 5F) relative to the quartz and clay dominated laminae.

Summarised, the fabric analysis shows that the Posidonia Shale Fm is predominantly composed of a stacked succession of mud-sized dominated thin beds often characterised by three internal units: a) a silt-dominated unit which is either gradually fining upwards or is arranged in low angle cross-laminae; b) a unit which consists of lamina sets of clay and silt dominated layers which are either horizontal or curved and vary from continuous to discontinuous; and c), a homogeneous and clay dominated unit which is predominantly recognised in the upper part of the Posidonia Shale Fm. The base of these thin beds often consists of an erosional base whereby microscour features and abrupt grain size difference are present.

4.2 Geochemistry

4.2.1 Carbon and sulfur isotope ratios, TOC and aluminum

In core L05-04 the S-isotope curve[2] shows a pronounced negative excursion to ca. -34 ‰ in the Aalburg Fm, and concomitantly, TOC[2] values gradually start to increase to ca. 4 % (figure 6). In the Aalburg Fm and lowermost Posidonia Shale Fm $\delta^{13}C_{org}$ ratios[2] vary around a value of ca. -27 ‰. At a depth of ca. 2766.0 mbsf the C-isotopes rapidly decrease towards highly negative values with a maximum of 32.4‰ at a depth of 2760.2 mbsf. The rapid decrease in C-isotope values is simultaneous with a significant increase in TOC and S-isotope values and a decrease in aluminium values. A maximum TOC content in the Posidonia Shale Fm of 16.2 % is reached at 2760.2 mbsf and S-isotope values increase to ca. -14 ‰ in the uppermost Posidonia shale Fm.

[2] Msc. thesis of Abhinav Singh Gill, 2006: Organic geochemical assessment of the Posidonia Shale in the Netherlands. Conducted at TNO Built Environment and Geosciences in collaboration with Utrecht University and GFZ German Research Centre for Geosciences.

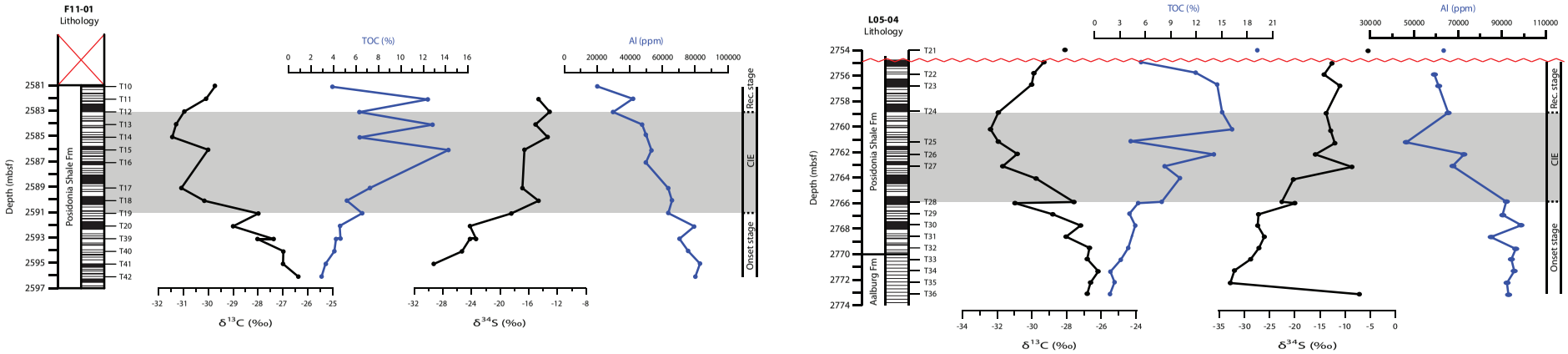

Figure 6

Left panel corresponds to well F11-01 and right panel to well L05-04. Shown are the δ13Corg isotope ratios, Total Organic Carbon percentage (TOC), δ34S isotope ratios and aluminum (Al) contents. The correlation is based on all four curves after the three stages identified by Cohen et al. (2007). The actual negative carbon isotope excursion (CIE) is indicated by the grey arced area. The CIE is predated by a onset stage starting simultaneously with the negative sulphur isotope excursion which is only sampled in well L05-04. The CIE is postdated by a recovery stage to pre -excursion values but is in both cores not completely sampled.

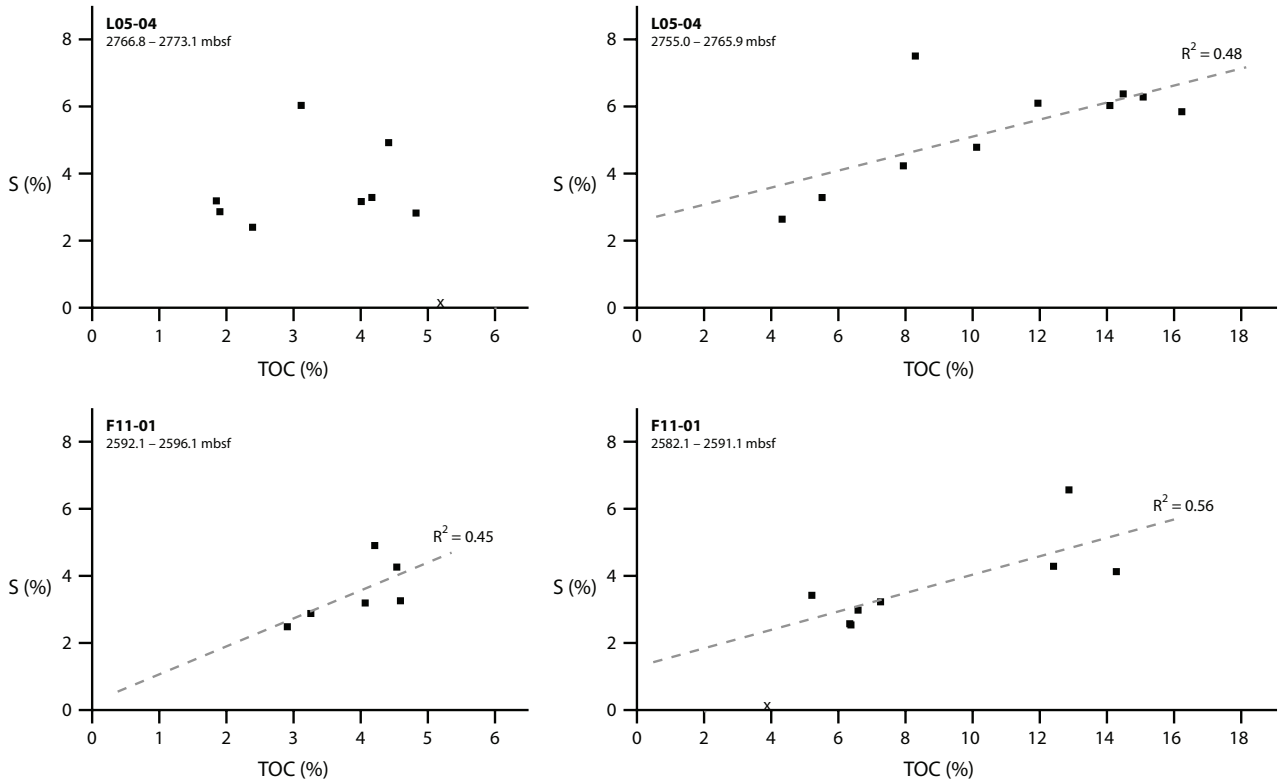

Figure 7

TOC versus S graphs. The left hand side graphs show the interval which correspond with the onset stage in the carbon isotopes, the right hand side graphs correspond with the carbon isotope excursion plus the recovery stage. The x labelled data points are left out of the correlation as the sample consisted for > 90 % of carbonate.

In core F11-01 the pronounced negative excursion in the S-isotopes and the simultaneous onset of the gradually increasing TOC values is expected to occur in the Aalburg Fm which has not been sampled (figure 6). The $\delta^{13}C_{org}$ isotope ratios show in the lowermost Posidonia Shale Fm some variation superimposed on a gradual increase. At a depth of ca. 2591.5 mbsf there is a rapid decrease in C-isotope ratios to a minimum of -31.5 ‰ at 2585.1 mbsf. Concomitantly, there is a significant increase in TOC values and S-isotope values and decrease in aluminium values. This is the same trend as in core L05-04. A maximum TOC value of 14.2 % is recorded at 2587.1 mbsf and S-isotope ratios increase to ca. -15 ‰ in the uppermost Posidonia Shale Fm. Furthermore, aluminium values are much lower in the uppermost Posidonia Shale Fm of core F11-01(20000 ppm) relative to L05-04 (60000 ppm).

A tentative correlation has been made between the cores of wells L05-04 and F11-01 based on the low resolution curves of $\delta^{13}C_{org}$ and $\delta^{34}S$ isotope ratios, TOC and aluminium (Al) content. Three stages, after Cohen et al. (2007), have been identified and used to correlate the curves. The first stage encompasses a little variation in C-isotopes superimposed on a gradual decrease, stage two incorporates the large and rapid shift in C-isotopes, the actual negative C-isotope excursion (CIE), and stages three is the recovery stage to average C-isotope values. The $\delta^{34}S$ isotope ratio, TOC and Al curves are correlated with the same three stages.

With the use of TOC versus S plots (figure 7) the redox boundary within a sedimentary environment can be estimated (Leventhal, 1983; Raiswell and Berner, 1985). For both cores a subdivision has been made between the onset stage, the lower part of the Posidonia Shale Fm, and the CIE plus recovery stage, the upper part of the

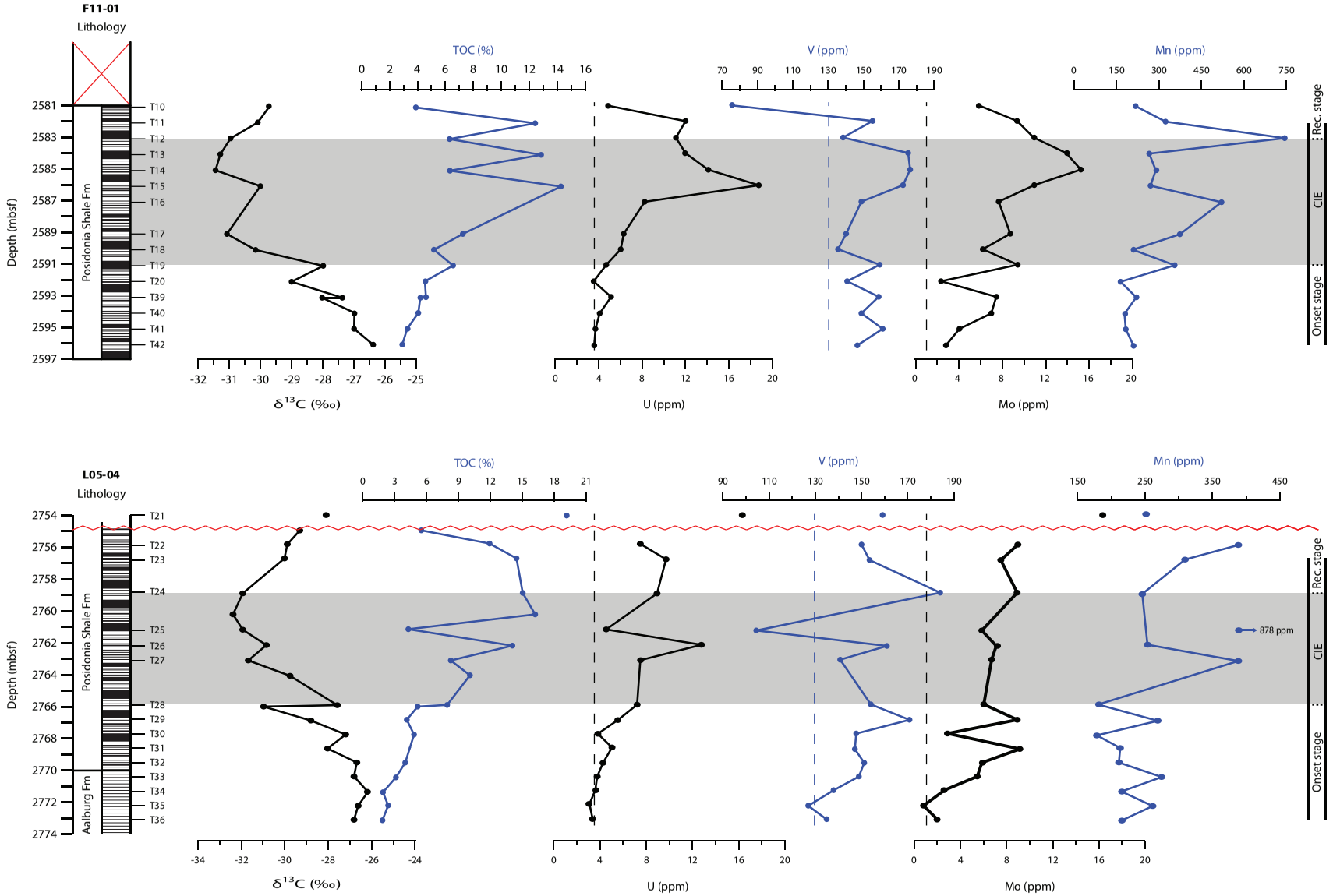

Figure 8

The top panel represents well F11-01 and the bottom panel well L05-04. The graphs show δ13Corg isotope ratios, TOC percentage, and the redox sensitive elements U, V, Mo and Mn. The vertical dashed lines represent average shale values (Wedepohl, 1971; Wedepohl, 1991). The correlation stages are after figure 6.

Posidonia Shale Fm. Correlations are relatively good for well F11-01 and the upper part of well L05-04, while correlation is almost absent in the lower part of L05-04. Important in these graphs is the observations that the trend line in both the upper parts in well L05-04 and F11-01 has a positive S intercept for a zero C intercept.

4.2.2 Paleoredox proxies

Redox sensitive elements have a tendency to be more soluble under oxidising conditions than under reducing conditions which results in enrichments in oxygen-depleted sedimentary facies. Therefore, uranium (U), vanadium (V), molybdenum (Mo) and manganese (Mn) are useful to examine oxygenation (Brumsack, 2006; Tribovillard et al., 2006). The average shale values used are from Wedepohl (1971; 1991).

In core L05-04 the elements U, V, Mo are slightly enriched compared to average shale values, while Mn is depleted relative to average shale values (figure 8). U, V and Mo values start increasing at the same depth as TOC values start increasing. Largest enrichments compared to average shale values are recorded in the actual negative C-isotope excursion. Mn values start to increase at the same level as the negative C-isotope excursion, but remain well below average shale values. High TOC values (2762.2 mbsf and 2760.2 – 2756.8 mbsf) coincide with the highest enrichments in the elements U, V and Mo, while at the low TOC value at 2761.2 mbsf the elements U, V and Mo are depleted and Mn enriched.

The redox elements in core F11-01 show similar trends as core L05-04 (figure 8). The elements U, V and Mo are enriched relative to average shale values and Mn is depleted relative to average shale values. In the lower Posidonia Shale Fm U and Mn are relatively stable around a value of 4 and 220 ppm respectively, while V and Mo vary superimposed on a gradual increase. The element concentration of U, V, Mo and Mn record significant enrichment at the level of the negative C-isotope excursion. Similar to core L05-04, high TOC values coincide with enrichments in U, V and Mo and depletions in Mn, while low TOC values coincide with depletions in U, V and Mo and enrichment in Mn.

4.2.3 Paleoproductivity proxies

Certain elements are predominantly delivered to the sediment is association with organic matter and, therefore, are good proxies for reconstructing paleoproductivity. These elements are nickel (Ni), copper (Cu), cadmium (Cd), zinc (Zn), barium (Ba) and phosphorus (P) (Tribovillard et al., 2006). The average shale values used are from Wedepohl (1971; 1991).

In core L05-04 the concentrations of the elements Ni, Cu, Cd and Zn start to increase simultaneously, from average shale values, with TOC in the Aalburg Fm (figure 9). Ba shows a decreasing trend and is depleted relative to average shale values. High TOC concentrations (2762.2 mbsf and 2760.2 – 2756.8 mbsf) coincide with enrichments in all six elements used here as proxies for productivity, while a relative low TOC concentration at 2761.2 mbsf coincides with a depletion of these elements. P concentrations show various enrichments and depletions superimposed on a average concentration of ca. 800 ppm.

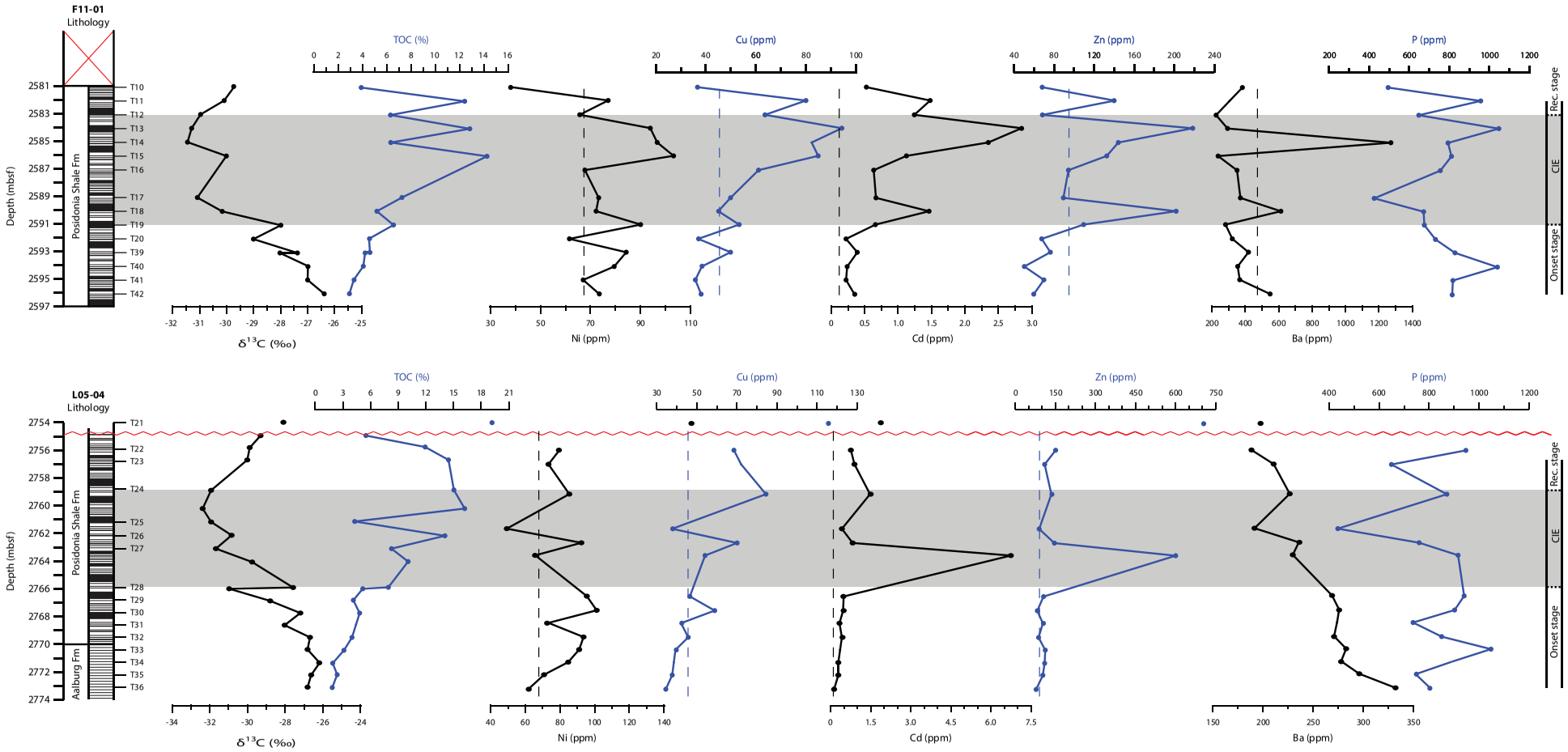

Figure 9

The top panel represents well F11-01 and the bottom panel well L05-04. Shown are $\delta^{13}C_{org}$ isotope ratios, TOC percentage and the productivity elements Ni, Cu, Cd, Zn, Ba and P. The vertical dashed lines represent average shale values *(Wedepohl, 1971; Wedepohl, 1991)*. The correlation is after figure 6.

In core F11-01 the elements Ni, Ba and P show various enrichments and depletions superimposed on an average concentration (figure 9). This average value is for Ni slightly above average shale values and for Ba well below average shale values. Cu and Cd concentrations show an gradual increasing trend, like TOC, from approximately average shale values and a rapid enrichment in the negative C-isotope excursion interval. Zn concentrations record a similar trend as Cu and Cd, but concentrations in the lowermost Posidonia Shale Fm start increasing from below average shale values. Furthermore, a trend whereby high TOC concentrations coincide with enrichments in Ni, Cu, Cd, Zn and P is recognised, while, in contrast with core L05-04, Ba shows its largest enrichments when TOC is low.

5. Discussion

5.1 Detrital components

The fabric analysis shows that the Posidonia Shale Fm is predominantly composed of a stacked succession of mud-sized dominated thin beds often characterised by three internal units. These thin beds are <10 mm thick and only recognised on high resolution flatbed scans. Because of these small parting spacings these layers can easily be mistaken for laminae. However, the scans show that the base of each thin bed is erosional as microscour features in combination with an abrupt change in grain size and fabric are present. Therefore, following the definition of genetic beds (after Campbell, 1967), the observed beds represent individual depositional events separated by breaks in sedimentation, and the use of this term in recent other studies describing similar fine-grained sedimentary rocks (e.g. Macquaker et al., 2007; Macquaker et al., 2010) it can be concluded that the use of the term "thin beds" is appropriate.

Fine grained detrital clay constitutes the bulk of the Posidonia Shale Fm in both cores. In addition to these fine-grained siliclastics, silt-sized quartz is a major component in the lower part of the succession. Both cores are composed of a stacked succession of thin beds and each thin bed is characterised by a tripartite stratigraphy consisting of: a) a silt-dominated unit which is either gradually fining upwards or is arranged in low angle cross-laminae; b) a unit which consists of lamina sets of clay and silt dominated layers which are either horizontal or curved and vary from continuous to discontinuous; and c), a homogeneous and clay dominated unit which is predominantly recognised in the upper part of the Posidonia Shale Fm. The base of these thin beds often consists of an erosional base whereby microscour features and abrupt grain size difference are present.

The basal unit of each thin beds is, thus, silt-dominated and its thickness varies from several mm in the lower part and often <1 mm thick in the upper part of the Posidonia Shale Fm. The erosional surfaces, recognised by micro-scour features and abrupt grain size changes, in combination with low angle or sub-parallel cross laminae and convolute lamination are indicative for bottom current processes in a high energetic environment of fine-grained sedimentation. Similar sedimentary structures are described in the Toarcian shales from Yorkshire (O'Brien, 1990), in the mud-substrate of shallow water coastal deposits of Surinam (Rine and Ginsburg, 1985) and the Mid-Proterozoic shales of Montana are interpreted by Schieber (1986) as storm dominated tidal environments in water only a few tens of meters deep. MacQuacker et al. (2010) interpreted similar structures as being the product of wave influenced, turbulent depositional conditions with a traction component. The presence of few small scale bioturbuation features in this unit indicates that there was only limited time and oxygen for infaunal communities to colonise the sediment surface, suggesting a high rate of sediment accumulation (Goldring et al., 1991; Macquaker et al., 2007) or a rapid redevelopment of anoxic conditions. Higher in the stratigraphy some detrital dolomite is recognised in these silt-sized layers. The dolomite clasts constitute of only a few grains and are angular of shape which suggests they are the product of erosion of cemented dolomite layers updip. In addition, the horizons with such dolomite clasts are not characterised by the presence of abundant pyrite such as the layers where dolomite is diagenetic and formed by bacterially mediated processes.

A fabric change, implying a change in depositional conditions, occurs between the basal unit and the second unit in each thin bed. The fabric changes from a predominantly silt-sized fabric to a fabric characterised by lamina sets of silt and clay dominated layers. The lamina sets are either horizontal or curved and vary from continuous to discontinuous. The grain size differences in the adjacent laminae reflect fluctuations in energy conditions. The coarser layers are deposited in shallow near-shore waters in higher energy, similar to bedding features in the Kimmeridge Clay at Dorset (England), and are probably the result of storm activity (Wignall, 1989). Finer-grained sediments are deposited during quieter periods between storm events (O'Brien, 1990). MacQuacker et al. (2010) state that the alternation of similar lamina sets is the result from the break-up of large flocs due to shear and mixing along the boundary between the mud suspension and the underlying coarser combined-flow deposits of wave enhanced sediment gravity flows. Both interpretations encompass the influence of wave activity in combination with variation in their energy level causing the alternation of silt and clay dominated laminae.

The third and uppermost unit within each thin bed is homogeneous and clay dominated with especially in the upper half of the Posidonia Shale Fm a preferred horizontal orientation of the clay particles. This unit represents periods with waning wave activity in which the water was quiet and bottom currents were absent, so clay particles could settle from suspension. The preferred orientation of the individual clay particles suggests that bioturbation was absent and conditions were likely anoxic. In the lower parts of both cores this unit is very thin or even absent which can point to many reasons. Among these reasons it is possible that erosion was more intense and dug deeper into the previously deposited sediment. This can be the result of lower sea level and the subsequent increase in wave dissipation at the seafloor. Another possibility is climatological, storms could be more intense or more frequent during deposition of the lower part of the Posidonia Shale Fm and resulted in only short periods of flow relaxation. Macroscopic lamination is absent in these unit, because mineralogical differences are not present.

5.2 Biogenic Components

Based on Rock Eval pyrolysis[3], a transition of organic matter origin in the Posidonia Shale Fm is recognised. The samples in the lower part have a hydrogen index < 300, while the samples in the upper part have a hydrogen index of 400 – 600. Furthermore, in most thin sections of the upper part of the Posidonia Shale Fm algae cysts are very abundant and are the most abundant biogenic element in the whole Posidonia Shale Fm. This implies that the lower part is predominantly characterised by terrestrial organic matter and shifts to marine dominated organic matter in the upper part of the succession. A similar shift in organic matter origin is noticed in the Toarcian sediments of SW Germany (Rohl et al., 2001; Schouten et al., 2000). Some sporadic shell fragments or bone fragments are recognised, however, these are always completely pyritised. The extremely low abundance of biogenic features point to a harsh environment in which these communities were not able to develop. This in combination with the high concentration of organic matter preserved points to anoxic conditions and the pyritization of the various bio-fragments to sulphidic conditions in the sediment.

[3] Msc. thesis of Abhinav Singh Gill, 2006: Organic geochemical assessment of the Posidonia Shale in the Netherlands. Conducted at TNO Built Environment and Geosciences in collaboration with Utrecht University and GFZ German Research Centre for Geosciences.

5.3 Diagenetic components

In the upper part of the Posidonia Shale Fm dolomite is mainly present as carbonate microconcretion layers together with a high abundance of pyrite framboids and euhedral crystals. The large sizes (up to ~30 μm) of the dolomite rhombs making up the microconcretions with respect to the surrounding clay-rich sediment indicates an authigenic origin (Pye and Krinsley, 1986). These carbonate cements are easily precipitated because of increased pore water bicarbonate, iron and sulphide activities as a result of bacterially mediated organic degradation. Especially ferroan carbonates and pyrite are the product of bacterial sulphide reduction, iron reduction and methanogenesis (Machel, 2004; Macquaker et al., 2007; Mazzullo, 2000; Taylor and Macquaker, 2000). However, most dolomite is non-ferroan which suggest that the majority of the iron is incorporated in the pyrite. In order to provide the pore space with the products of this bacterial metabolic activity it is likely that these surfaces were close to the sediment-water interface for prolonged periods indicating periods with breaks in sedimentation (Coleman et al., 1985; Irwin et al., 1977; Macquaker et al., 2007; Raiswell, 1987). Allowing time for these carbonate microconcretions and pyrite to precipitate and the absence of thick carbonate concretions suggests that breaks in sedimentation were relatively short (Macquaker and Gawthorpe, 1993) and/or sedimentation rate was probably intermittent (Bottrell and Raiswell, 1989).

5.4 Geochemical conditions

The enrichment in heavier sulphur isotopes in the uppermost Aalburg Fm is concomitant with the onset of increasing TOC content (> ~1 %). The process of bacterial sulphate reduction is associated with a isotope fractionation, with the product sulphide being depleted in the heavier isotope ^{34}S (Meyer and Kump, 2008). The light $\delta^{34}S$ isotope ratios in the base of the Posidonia Shale Fm suggest that the majority of sulphide was produced in the surface layer and that the TOC content was insufficient to continue sulphate reduction in the zone of diffusion. A value of ~ -35 ‰ represents open system fractionation and indicates a limited amount of organic matter available for degradation. The shift to heavier isotope ratios is simultaneous with a rapid increase in TOC. This likely represent a high contribution of close system fractionation which was possible due to increase preservation and, thus, availability of organic matter for bacterial sulphate reduction (Fisher and Hudson, 1987; Lyons et al., 2009). Brumsack (1991) noticed a relation with heavier sulphur isotope values and carbonate enrichment and explained this by an increased accumulation rate of mainly coccoliths making the system more closed with respect to sulphate. The carbonates in the upper part of the Posidonia Shale Fm in the DCG are mainly diagenetic microconcretions and prevented diffusion from overlying seawater in the pore waters resulting in a more closed environment and heavier isotope values. Heavy isotope ratios and, thus, intense sulphate reduction often indicate sulphidic basins (Meyer and Kump, 2008). This increased bacterial sulphate reduction can also be reflected in the more abundant pyrite framboids, euhedral pyrite crystals and diagenetic dolomite in the upper part of the Posidonia shale Fm.

The TOC versus S plots can be used to determine the position of the redox boundary within a sedimentary environment (Fisher and Hudson, 1987; Leventhal, 1983; Raiswell and Berner, 1985). Sulphidic conditions in the bottom water are very likely as the TOC/S correlation shows a positive S intercept for a zero C intercept. The

results show that correlation is either absent or has a zero S intercept for a zero C intercept in the lower part of the Posidonia Shale Fm in both cores. For the upper part, however, a correlation with a positive S intercept is recognised. This suggests that bottom water conditions were not anoxic during deposition of the lower part of the Posidonia Shale Fm, but likely were anoxic or even sulphidic during the carbon isotope excursion. Rohl et al. (2001) did a similar analyses for the black shales in SW Germany, only higher up in the stratigraphy, and concluded that it proved to be a very useful tool to estimate paleo oxygen levels independently. However, short term oxygen events can not be recognised with this technique.

The overall trend in trace metal concentrations is an enrichment, relative to average shale values, for both the redox and productivity proxies indicating increased anoxia and productivity in the upper part of the Posidonia Shale Fm. Extremely high metals concentrations, as have been found in other black shales (e.g. the Cenomanian/Turonian black shales), are not attained which is in agreement with the trace metal concentrations found by Brumsack (1991) in the German Posidonia Shale. In addition, the concentrations of the elements V, Mo, Cu, Cd, Zn and partly Ni are all within the data ranges of previous studies (Brumsack, 1991; Pye and Krinsley, 1986). Several elements (P, Ba, Zn and Cd) are relatively easily remobilised after deposition, while the elements U, V, Mo, Ni an Cu are the least vulnerable to primary and secondary processes and, therefore, most useful as paleoredox and paleoproductivity proxies (Tribovillard et al., 2006). The concurrent enrichment of the redox sensitive elements U, V an Mo in the upper part of the Posidonia Shale Fm very likely reflect anoxic to sulphidic conditions at the sediment-water interface or in the water column (Algeo and Maynard, 2004; Tribovillard et al., 2006). Ni and Cu are delivered to the sediment in association with organic matter. These elements are released by organic matter degradation and can be trapped in the sediment by pyrite if sulphate reducing conditions prevail. Hence, if Ni and Cu are not scavenged by settling organic matter particles, they will not be present in the sediments even if reducing condition develop rapidly. The enrichments of Ni and especially Cu higher in the stratigraphy indicate, therefore, that these elements were brought to the sediment in increased abundances and that reducing conditions were met, allowing Ni and Cu fixation in the sediment (Algeo and Maynard, 2004; Tribovillard et al., 2006).

5.5 Vertical and spatial patterns

The stacked succession of thin beds with, in general, an erosional base followed by a silt-sized dominated unit, an alternating silt clay laminated unit and on top a clay dominated unit represents periodic changes in depositional energy conditions. The basal unit of each thin bed represents a high energy event, possibly storm induced wave activity, causing small scale erosion and the subsequent deposition of the silt-sized unit. This is followed by fluctuating intermediate and low energy events likely generated by wave enhanced sediment gravity flows (Macquaker et al., 2010) or minor storm induced wave activity producing the alternating silt and clay dominated laminae. Finally, there is relaxation of the flow representing low energy periods with suspension settling of clay particles. This typical vertical trend in each thin beds suggests that the sediment-water interface was located below the fair-weather wave base, but in relatively shallow water above the storm wave base. The high energy events associated with the silt-sized units likely mixed oxygen-rich surface water with oxygen-deficient deeper water and subsequently caused short periods of oxic conditions near the sediment-water interface letting infaunal organisms colonise the sediment.

Superimposed on the internal thin bed zonation, the complete sedimentary succession shows a vertical upward trend in which the silt-dominated unit becomes thinner and the clay dominated unit becomes increasingly thicker. Furthermore, clay minerals tend to be more horizontally oriented higher up in the stratigraphy. The origin of the organic material shifts from terrestrial dominated to marine dominated organic matter and the aluminium content in both cores decreases upwards. This suggests a proximal setting during deposition of the uppermost Aalburg Fm and lower part of the Posidonia Shale Fm while it gets a more distal character higher up in the stratigraphy. This reflects a transgressive trend in which water depth increases with time and is consistent with reconstructed sea level curves (Hallam, 1981; Haq et al., 1987) which document a transgression during the Toarcian.

The upward enrichment in heavier sulphur isotopes, redox and productivity proxies and the concomitant increase of TOC concentration suggest an increasingly anoxic environment. This, the high abundance of pyrite in the upper part of the Posidonia Shale Fm, the carbonate microconcretions and the TOC vs S plots point to sulphidic conditions at the sediment-water interface and anoxic and possibly sulphidic conditions in the water column. However, these conditions did not prevail throughout the whole stratigraphic interval. The erosion features in combination with the silt-dominated, storm induced wave activity deposits likely caused periodic inflows of oxygenated waters. Oxygenation of the bottom water was only short term as there are only few indications of bioturbation in these layers.

In core L05-04 the silt dominated units are overall more pronounced with respect to core F11-01. In addition, aluminium concentrations are higher in the upper part and organic matter particles tend to be larger in core L05-04. These are subtle indications for a more proximal character of core L05-04 during deposition of the Posidonia Shale Fm. Another explanation is an already pronounced DCG in which core L05-04 was located near the margin and core F11-01 in the centre of the graben. These positions are similar to present-day geographical positions and can be considered as an option as the DCG was already a structural element since the mid-Carboniferous (Geluk, 2007; Glennie, 1990).

5.6 Wider implications

By comparing the Toarcian black shales of the DCG, Yorkshire and SW Germany it is evident that the geochemical signature is, in general, similar in all three localities. Organic geochemical studies of Rohl et al. (2001), Farrimond et al. (1989), and Schouten et al. (2000) all record the negative carbon isotope excursion and the concomitant increase in TOC concentration. Furthermore, these studies show a similar shift from terrestrial to marine organic matter at the same moment in time. Brumsack (1991) showed similar sulphur isotope trends and both Brumsack (1991)and Pye and Krinsley (1986) found similar values and trends for redox and productivity proxies in the Posidonia Shale of SW Germany and Yorkshire.

Although general mineralogical differences are not present, the interpretation of the texture and fabric is different in these localities. O'Brien (1990) studied the sedimentary structures of the Toarcian shales of Yorkshire. His results point out that the Jet Rock Shales are characterised by a combination of wavy lamination

and thick lamination. The wavy laminae are interpreted to be the remains of benthic microbial mats, while the thick lamination is associated with bottom current activity. Pye and Krinsley (1986) identified a fine lamination predominantly composed of detrital quartz and clay, and diagenetic pyrite and carbonates. They conclude that the Jet Rock facies indicate a carbon-rich sulphidic environment which extended up to the sediment surface. Rohl et al. (2001) found in the sedimentary fabric of the Oil Shales of SW Germany microlamination which consists of alternating argillaceous, organic-rich laminae and pellet-rich laminae. In the lower part of the Oil Shales an irregular filamentous network surrounding the pellets is observed which seem to be the relicts of microbial mats. Furthermore in this lower part of the SW German Oil Shales, rare and thin silty layers, characterised by a sharp base, are found and interpreted to represent distal storm deposits or turbidites which result from very brief events that just reached the deeper parts of the basin.

The findings summarised above are, however, in agreement with the findings of this study. The interpretation of the sedimentary structures of this study, based on the three-fold internal stratigraphy of the thin beds, points to changing depositional conditions. The first unit is characterised by a high energy event , possibly storm induced wave activity, causing small scale erosion and the subsequent deposition of the silt-sized unit. Both O'Brien (1990) and Rohl et al. (2001) report these similar silt dominated layers with a sharp or even erosional base for Yorkshire and SW Germany and conclude that these layers are the result of short periods of relatively high energy conditions. The second unit encompasses fluctuating intermediate and low energy events likely generated by wave enhanced sediment gravity flows (Macquaker et al., 2010) or minor storm induced wave activity producing the alternating silt and clay dominated laminae. Mineralogically comparable laminated sediments have been recognised in Yorkshire by Pye and Krinsly (1986) and O'Brien (1990). Furthermore, O'Brien (1990) mentioned sediments composed of parallel carbonaceous flakes and other platy material which are deposited by suspension settling. These sediments have many similarities with the homogeneous clay units recognised in the DCG which are associated with suspension settling during low energy periods. A sedimentary feature not recognised in the DCG, but present in both SW Germany and Yorkshire, are remains of microbial mats. Because not a single thin section shows any evidence for their presence in the DCG, it is likely that condition for microbial mat development were unfavourable, however, the data presented here suggest an anoxic environment with sulphide being present which are conditions associated with microbial mat growth (Cohen et al., 1975). Overall, it can be concluded that the characteristics of the separate units of the thin beds in the DCG are recognised in both Yorkshire and in SW Germany and, thus, the results of this study are in agreement with similar sediments in NW Europe. In addition, the transgressive trend superimposed on the stacked succession of thin beds recognised in the DCG is also recognised in Yorkshire and SW Germany.

The geochemical results of this study point to anoxic conditions in the sediment during the lower part of the Posidonia Shale Fm and which intensified to anoxic to sulphidic bottom water conditions during deposition of the upper part of the Posidonia Shale Fm. These intensified anoxic to sulphidic bottom water conditions are concomitant with the negative carbon isotope excursion, very high TOC concentrations and increasingly heavier sulphur isotopes. According to Brumsack (1991) the geochemistry of the SW German sediments represent deposition in a shallow epicontinental sea with likely a fluvial influence resulting in oxic surface waters overlying more saline anoxic deeper waters and, therefore, water column stagnation. In addition, the sulphur isotope curve

of SW Germany is similar to the curve presented in this study with the isotonically light values in the lower part and the isotopically heavier values in the upper part. Based on the geochemical results alone the depositional environment of the DCG would be similar to the depositional environment described by Brumsack (1991) for SW Germany. However, the finding of the sedimentary and petrographic analyses show that this is not true. The systematic macro- and micro-sedimentary analyses showed that the Posidonia Shale Fm is characterised by a stacked succession of thin beds with an erosional base and a silt-dominated basal unit. This silt-dominated unit is associated with storm induced wave activity and the subsequent overturning of the water column and inflow of oxygen-rich water. This conclusion, that the Toarcian black shales are deposited in an anoxic to sulphidic environment with a periodically overturning of the water column and the subsequent inflow of oxygen-rich water, is in agreement with recent other studies. Van de Schootbrugge et al. (2005) concluded on the basis of belemnite carbon isotopes that the anoxic waters were interrupted by brief return to a fully oxygenated state following overturning of deeper waters. Rohl et al. (2001) concluded on the basis of palaeoecological, sedimentological and geochemical analyses the presence of extremely short oxygenation periods characterised by colonisation events.

This study proves, therefore, that it is important to use a combination of optical/electron optical and geochemical analyses to determine depositional conditions. Especially of importance are the use of macro scale sedimentary analyses. Mainly this analysis led to the conclusion that the Posidonia Shale Fm is characterised by a stacked succession of thin beds with a three-fold internal stratigraphy. Although many similar sedimentary characteristics are observed in Yorkshire and SW Germany, the macro scale sedimentary sequence as has been presented here has not been described in these studies. The combined optical/electron optical and geochemical analyses of the Posidonia Shale Fm led to the conclusion that depositional conditions changed from only anoxic conditions below the sediment-water interface in the lower part of the Posidonia Shale Fm to anoxic to sulphidic bottom water conditions in the upper part of the Posidonia Shale Fm. The three-fold internal stratigraphy, however, showed that these conditions were interrupted by short events, possibly by storm induced wave activity, and the subsequent inflow of oxygen-rich surface waters. The Posidonia Shale Fm is, thus, deposited in a dynamical fine-grained sedimentary environment periodically characterised by alternating conditions of bottom currents causing erosion and other flow associated sedimentary structures, and relaxation of the flow resulting in laminated sediments or even homogeneous clay layers. Although the presented interpretation of the sedimentary sequence is different from studies of the NW European Toarcian black shales, the overall conclusion on the depositional conditions are in agreement with recent other studies (Rohl et al., 2001; Van de Schootbrugge et al., 2005).

6. Conclusion

The Posidonia Shale Fm is characterised by a stacked succession of mud-sized dominated thin beds often characterised by three internal units. These thin beds have an erosional base with on top a silt-dominated unit which is either gradually fining upwards or arranged in low angle laminae. The second unit consists of lamina sets of clay and silt dominated layers which are either horizontal or curved and vary from continuous to discontinuous. The uppermost unit, which is predominantly recognised in the upper part of the Posidonia Shale Fm, is homogeneous and clay dominated. Superimposed on the internal thin bed zonation, the complete sedimentary succession shows a vertical upward trend which reflects a transgressive trend with a proximal setting during deposition of the uppermost Aalburg Fm and lower part of the Posidonia Shale Fm while it gets a more distal character higher up in the stratigraphy. Furthermore, the upper part of the Posidonia Shale Fm is characterised by carbonate micro concretions and a high abundance of pyrite. The geochemical analyses shows a concomitant negative carbon isotope excursion, increase in TOC concentration and an increasingly heavier sulphur isotope trend. Furthermore, redox and productivity proxies are enriched in the upper part of the Posidonia Shale Fm.

The three-fold internal stratigraphy of each thin bed led to the conclusion that depositional conditions changed periodically. The basal unit of each thin bed represents a high energy event, possibly storm induced wave activity, causing small scale erosion and the subsequent deposition of the silt-sized unit. This is followed by fluctuating intermediate and low energy events likely generated by wave enhanced sediment gravity flows or minor storm induced wave activity producing the alternating silt and clay dominated laminae. Finally, there is relaxation of the flow representing low energy periods with suspension settling of clay particles. This typical vertical trend in each thin beds suggests that the sediment-water interface was located below the fair-weather wave base, but in relatively shallow water above the storm wave base. The high energy events associated with the silt-sized units likely mixed oxygen-rich surface water with oxygen-deficient deeper water and subsequently caused short periods of oxic conditions near the sediment-water interface letting infaunal organisms colonise the sediment.

This in combination with the geochemical analyses led to the overall conclusion that only anoxic conditions below the sediment-water interface prevailed in the lower part of the Posidonia Shale Fm and extended to anoxic to sulphidic bottom water conditions in the upper part of the Posidonia Shale Fm. The three-fold internal stratigraphy, however, showed that these conditions were interrupted by short events, possibly by storm induced wave activity, and the subsequent inflow of oxygen-rich surface waters. The Posidonia Shale Fm was, thus, deposited in a dynamic environment with an alternation of anoxic and short-term oxic conditions.

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