



Climate forcing of fine-grained deep-marine systems in an active tectonic setting: Middle Eocene, Ainsa Basin, Spanish Pyrenees



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ABSTRACT

A multi-proxy approach to understand environmental change in deep time was undertaken on about 150 m of core from a 230 m-long Middle Eocene core from the Ainsa basin, Spanish Pyrenees, representing deep-marine siliciclastic sediments, using detailed sedimentary logging, high-resolution multi-element XRF geochemistry, total organic carbon, and stable carbon isotopes. The Well A6 was drilled, as part of an industry–university consortium, through siltstones, fine-/very fine-grained sandstone turbidites, and hemipelagic structureless mudstones, that were deposited as overbank and off-axis deposits from a sandy submarine fan, and interfan deposits. For comparative mineralogy between the sandstone turbidites and siltstones, scanning electron microscopy (SEM) and X-ray diffraction (XRD) were undertaken on selected samples. The sandstone turbidites show enrichment of detrital elements such as Si, Zr and Ti, that can be linked to greater quartz and heavy-mineral content compared with adjacent siltstones. Structureless hemipelagic mudstones comprise mainly clay minerals and carbonate. We interpret the sandstone turbidites as from hyperpycnal flows during high river sediment discharge, whilst hemipelagic mudstones resulted from the suspension fall-out of hypopycnal flows. Cyclostratigraphic analysis of the core reveals Milankovitch cyclicity at frequencies of ~0.03 cycles/m (short eccentricity), ~0.09 cycles/m (obliquity), ~0.15 cycles/m (precession couplet) and ~0.19 cycles/m (precession couplet). Orbital parameters appear to have controlled the cyclic delivery of coarser-grained sediment by turbidity currents. Two equally plausible depositional models, both as Milankovitch-driven, can explain the cyclical changes in the deep-marine sediments: (1) climatic cycles, with humid periods of enhanced chemical weathering, increased storminess and greater riverine run-off, leading to high sediment flux to the deep basin as sandstone turbidites; (2) climatic cycles, with cooler conditions linked to high-frequency small-scale eustatic sea-level fluctuations, with lowstand shelf-edge delta progradation, resulting in greater volumes of coarse detrital sediment to the seafloor by hyperpycnal flows. This study provides an insight into the likely depositional effects of orbitally-induced climate change on the nature and delivery of terrigenous sediment into deep-marine environments.

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1. Introduction

Whilst many studies have demonstrated the importance of global climate change as a major driver for cyclic depositional patterns in pelagic and hemipelagic sediments in deep time, there remains considerable controversy about its significance for deep-marine siliciclastic deposits, i.e., the role of climate, tectonic and/or autocyclic processes, particularly in tectonically active sedimentary basins. In order to try and understand better the underlying causes for cyclic deposition of sandy deposits in a tectonically active basin, we have undertaken a detailed sedimentological study of an essentially fine-grained siliciclastic deep-marine sedimentary record from an ~150 m-long core record drilled in Middle Eocene deposits in the Spanish Pyrenees. We also use multiple geochemical proxies to infer variations in grain size, weathering, organic content, and the geochemistry of the three main

lithologies, sandstone, siltstone and mudstone. TOC and stable carbon isotope studies are also included in our study as they provide a useful means for likely identifying the origin of organic matter and characterising the nature and provenance of the sediments in the basin.

The geochemistry of ancient deep-marine sediments provide important information on sediment sources (e.g., Heller and Frost, 1988; McLennan et al., 1993), sediment transport processes, palaeoclimatic and palaeoenvironmental conditions such as fluctuations in biological productivity and the redox state of bottom waters (Stein et al., 1989; Shimmield and Mowbray, 1991; Salami and Zachos, 1999; Werne et al., 2000). Geochemical proxies are commonly used to deduce the likely environment of the formation of deep-marine sedimentary rocks (Feng and Kerrich, 1990; Calvert and Pedersen, 1993; Schneider et al., 1997; Schnetger et al., 2000). Individual proxies have their limitations and therefore, a multi-proxy approach is preferred to obtain a comprehensive understanding of palaeoenvironments.

Analysis of deep-marine fine-grained thin-bedded turbidite and hemipelagic deposits provides an opportunity to interrogate

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sedimentation patterns, because this combines both a terrigenous detrital component (represented in the delivery of clays and terrestrial organic matter), and a pelagic biogenic component containing mineralised skeletal remains and marine organic matter. Additionally, the authigenic component reflects the burial and diagenetic history. Both the terrigenous and biogenic components are sensitive to climate. The terrigenous component, mainly fluvial and aeolian, is affected by changes in precipitation, erosion, and weathering. Also, relative sea-level changes can alter the amount and path of the sediment being transported to a basin. The biogenic component is sensitive to water column conditions that affect productivity. Climate can also influence the biogenic influx by regulating nutrient supply and by controlling water-column stability (e.g., [Werne et al., 2000](#); [Moreno et al., 2002](#)). Tectonic processes can also exert a major control on the terrigenous and biogenic component via tectonic uplift/subsidence and basin accommodation space which, in turn, will affect rates of weathering and erosion and may cause relative sea-level changes. Deconvolving climatic and tectonic processes preserved in geochemical records can, therefore, be very challenging.

Cyclostratigraphic techniques are routinely employed to determine the potential presence of orbital cycles in marine sediments (e.g., [Boyd et al., 1994](#); [Reijmer et al., 1994](#); [van Buchem et al., 1994](#); [Sageman et al., 1997](#); [Pälike et al., 2001](#); [Heard et al., 2008](#); [Gómez-Paccard et al., 2011](#); [Hodell et al., 2013](#)). Climate is affected by the variations in the amount and distribution of incoming solar radiation which are ultimately controlled by orbital cycles. Eccentricity, obliquity and precession cycles, therefore, affect sedimentation patterns as they can cause cyclical climatic variations with known periodicities. The link between orbitally forced climatic variability and sedimentation is still poorly understood ([Meyers and Sageman, 2000](#)). We have applied cyclostratigraphic techniques to high resolution geochemical data of a continuous hemipelagic and thin-bedded, fine-grained turbidite stratigraphic record to help our understanding of how these orbital cycles have affected the detrital and biogenic flux to deep-marine environments.

2. Methods

2.1. XRF scanning

Well A6 core was scanned using a multi element XRF Avaatech scanner sited at University College London (UCL). A 170 m long, essentially continuous, core length was scanned from 230 to 60 m depth below the surface using a core spacing interval of 4 cm between measurements. This section avoids the top 60 m of chaotic sediments of the A6 core (type I MTC, [Pickering and Corregidor, 2005](#)). At ~71 m depth, pronounced peaks in the natural gamma and in several XRF elements (Supplementary material 1) have been associated to ~10 cm duplex structure. Below this tectonically deformed zone, there are two intervals of chaotic deposits or mass-transport deposits (MTDs) ~1 m thick at 74 and at ~80 m depth. In order to perform time-series analysis, we avoided using any sections with deformed intervals, and restricted our study to the undeformed section 230–80 m depth. A high-resolution sampling interval was selected to detect any high-frequency environmental changes using time-series analysis. The detection of cycles is defined by the Nyquist critical frequency which suggests a minimum of 2 samples per smallest oscillation to avoid aliasing in the time series, although many studies recommend a minimum of 8 samples per cycle in the period of the smallest oscillation ([Herbert, 1994](#)). Spectral studies of bioturbation intensity in the Ainsa basin suggest estimated sediment accumulation rates of ~30 cm/kyr ([Heard et al., 2008](#)), suggesting that 4 cm sampling interval would permit recognition of Milankovitch cycle cycles at the highest frequency of ~20 kyr.

A 31 m section, from 176 to 206 m depth, was scanned at a much higher resolution using a spacing interval of 3.5 mm. This spacing interval was selected to detect geochemical signatures of the cm-size

sandstone turbidites and structureless mudstone facies. The resolution of the system was set with a 2 mm slit window and a 30 second sampling time. A two-run excitation mode was set in order to obtain a wide range of spectral data. The first run was set at 10 kV and 800 mA and no filter was used. These settings were established to get reliable results for elements such as Al, Si, P, S, K, Ca, Ti, Fe and Mn. Elements such as Sr, Rb and Zr were effectively measured setting the scanner at 30 kV and 1000 mA with a PD thick filter. These instrument settings are recommended to obtain reliable data ([Richter et al., 2006](#)).

The A6 core was analysed in a polished and smooth horizontal surface to allow for the scanner prism to sit flat on the surface of the sediment, thereby reducing the presence of air which may cause interference on the spectral analysis. Where necessary, the sampling plan was adjusted to avoid fracture areas.

XRF data were processed using WinAxilBatch software. A processing model was selected to obtain counts for each element and WinAxilBatch calculated the element counts as peak integrals and applied background subtraction. Data quality was checked by examining the processed output data. Isolated high Chi-squared (χ^2) values above 3 were deleted as they indicate a poor fitting between the scanner spectrum data and the mathematical model chosen for processing the data. Conversion of total counts per second (cps) values to absolute concentration was not attempted as we are interested in the variation of element concentrations rather than absolute values. Elements such as Mo, V and Zn had very low cps close to the nominal sensitivity of the instrument and were, therefore, excluded from interpretation.

2.2. Total carbon (TC) and total organic carbon (TOC)

Total carbon (TC) and total organic carbon (TOC) were determined using a Flash EA Analyzer sited at University College London. A total of 142 samples were obtained from the working halves of Well A6 core at a 1 m stratigraphic interval. Sampling took place from 230 to 88 m core depth. This interval consist mainly of undeformed marlstones and thin to very-thin bedded turbidites.

To obtain TC, ~30 mg of the sample was weighed to obtain satisfactory CN chromatograph peaks. The analysis of TOC required 60 mg of the sample which was treated with HCl 10% to remove inorganic carbonate content and then dried on a hot plate at 50 °C for a minimum of 12 h prior to analysis. Standards were used at the beginning (to calibrate the equipment), during and at the end of the run to test for accuracy of the results. Calcium carbonate content was calculated following Eq. (1).

$$\text{CaCO}_3 = (\text{TC} - \text{TOC}) \times 8.333 \quad (1)$$

2.3. Carbon isotopes

Stable carbon isotopes of organic matter were measured in the UCL Bloomsbury Environmental Isotope Facility (BEIF) using a Flash EA 1112 mass spectrometer. The technique used for determination of $\delta^{13}\text{C}$ values is the EA-IRMS (Element Analysis–Isotope Ratio Mass Spectrometry). Samples were collected from 230 to 88 m core depth at the same intervals as the samples collected for TC and TOC analysis. The uppermost 88 m of the core, however, was not sampled due to the presence of a thrust zone at ~71 m depth and because of several MTDs present in the upper parts of the core. Although XRF analyses were made between ~230 and 80 m core depth, there was insufficient material for TC, TOC and stable carbon isotopes from 88 to 80 m core depth without using the archive half of the core. Preparation of the samples for stable carbon isotope analysis involved the treatment of the samples with HCl 10%. The high content of calcite cement in the samples required the use of at least three applications of HCl 10% to ensure digestion of all inorganic carbonate. The samples were centrifuged and the solution decanted. The samples were subsequently washed with

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