

PP41B-0842 0830h POSTER

Nitrogen Fixation Enhanced Organic Matter Production in Demerara Rise Black Shales

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The high concentrations of organic carbon that are common to Cretaceous black shales imply levels of sustained primary production that are unknown in the modern ocean. How organic matter productivity could be maintained for many millennia remains an open question. Cenomanian to Santonian black shale sequences in the five sites drilled by Leg 207 on the Demerara Rise range in thickness from 56m to 93m. The finely laminated sequences contain between 1 and 28 percent organic carbon, and their organic geochemical properties reveal aspects of the exceptional conditions of organic matter production and preservation involved in their formation. The results of Rock-Eval pyrolysis show that the bulk of the organic matter originates from marine primary production. Improved preservation of the organic matter is implied by C/N ratios that increase to 40 as organic carbon concentrations increase; land-plant organic matter appears to be important only in the lower Cenomanian black shales from Site 1260 in which C/N ratios sometimes reach 60. Nitrogen isotope compositions that become lighter as organic carbon concentrations increase indicate that organic matter production was enhanced by a consortium of primary producers that included nitrogen fixing bacteria. Expansion of an intensified oxygen minimum zone into the photic zone probably permitted coexistence of algae and the photosynthetic microbes that function best under dysaerobic and anaerobic conditions and that are not limited by nitrate availability.

PP41B-0843 0830h POSTER

Cretaceous Oceanic Anoxic Events and Radially Elongated Chambered Planktonic Foraminifera: Palaeoecological and Palaeoceanographic Implications

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Planktonic foraminifera with radially elongated chambers became a consistent component (up to 80%) of foraminiferal assemblages in coincidence with the deposition of the main prominent Cretaceous organic carbon-rich horizons. However, the exact ecological meaning of elongated chambered forms and related palaeoceanographic scenario are not definitively established. All this above moved us to investigate in greater detail on the elongated chambered planktonic foraminifera across the latest Hauterivian Faraoni Event, the late Early Aptian Selli Event (OAE1a) and the latest Cenomanian Bonarelli Event (OAE2) in different areas from the Mediterranean Tethys (Umbria-Marche Apennines as type area, Southern Alps, Gargano Promontory, Sicily, SE Spain, SE France). Our analysis, conducted both on washed residues and thin sections confirms that the radially elongated chambered forms preferred oxygen-depleted waters and provides the following main evidences: a) each events has its own peculiarities; b) there is not relationship between Corg accumulation and relative abundance of this foraminiferal group; c) the first radiation of elongated chambered morphotypes (i.e., *P. eocretacea*) remarkably just predates the Faraoni Event with the percentage of these forms not exceeding the 7%; d) the relative abundance of these forms across the Cretaceous anoxic events varies in the different studied areas, probably also controlled by the water depth. In particular, the development of radially elongated chambered forms across the Selli Event seems to be favoured in shallower settings; e) the three morphological categories established for the Early Cretaceous radially elongated chambered forms (sublavate to clavate chambers, pointed at the end chambers, bulbous terminations-bearing chambers) are present in the

investigated areas in variable percentages. This evidence suggests that local environmental parameters influenced their distribution. Remarkably, the particularly elongated subclavate to clavate morphotypes (i.e., *P. robesae*) appear almost restricted to the western Mediterranean Tethys; f) a possible competition between radiolaria and leupoldinids across the Selli Event is reflected by their distribution patterns showing evidence that the latter group became more abundant (up to 10%) when the former decrease in abundance or are absent. Conversely, the other subclavate to clavate forms do not seem to suffer the relative high abundance of radiolaria. All this above allow us to speculate that leupoldinids are the less eutrophic forms among the radially elongated chambered morphotypes proliferating under moderate degree of fertility; g) higher numbers of radially elongated chambered forms together with a more consistent distribution are recognized just after the Selli Event suggesting that this event played a fundamental role in the radiation of this planktonic foraminiferal group; h) the onset and end of the Bonarelli Event in deep-water settings is characterized by schackoinid assemblage-dominated (up to 80%). According to their morphological features, schackoinids appear more competitive than other radially elongated chambered forms in low-oxygen, eutrophic conditions; i) the remarkably higher percentages of radially elongate chambered forms across the Bonarelli Event may provide evidence that the intensity of the environmental perturbation related to the Cretaceous anoxic event was much stronger during this event and weaker during the Faraoni Event.

PP41B-0844 0830h POSTER

Calcification Changes of Mesozoic Calcareous Nannofossils

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Studies on plankton samples and cultures revealed a variety factors which presumably control calcification and the size of coccoliths. Among others temperature, nutrients and seawater pH are thought to influence nannoplankton calcification. Whereas these studies only provide information of very short time intervals from hours to years, global climatic and oceanographic changes occur, however, on geological timescales. Thus their impact on nannofossil calcification and carbonate production can only be studied from the fossil record. We investigated DSDP sites from the western Atlantic of late Jurassic to early Cretaceous age in order to better understand long-term variations of the size of common nannofossil taxa and the resulting carbonate accumulation. The studied interval is characterized by two events in the pelagic carbonate record: (1) the onset of pelagic carbonate accumulation in the Tithonian, and (2) the Valanginian 'nannoconid crisis'. The Tithonian event went along with high abundances of strongly calcified nannofossils which presumably have an affinity to more oligotrophic surface water conditions. The mid Valanginian is marked by a positive carbon isotope excursion (CIE). This coincides with a sea level rise, volcanic activity and elevated atmospheric pCO₂ levels. Greenhouse climate and an accelerated hydrological cycle presumably intensified weathering processes causing enhanced nutrient transfer from the continents into the oceans. Increasing surface water fertility is indicated by high abundances of nannofossils which possibly indicate more eutrophic conditions. In the western Tethys the CIE is predated by a sharp decrease in the abundance of rockforming nannoconids. This event is less pronounced in the western Atlantic due to a general scarcity of nannoconids. Low nannofossil carbonate accumulation rates and a dominance of less calcified taxa were observed and may reflect a general marine biocalcification crisis. Possible factors, which may have caused changes in calcification and carbonate accumulation are (1) the trophic system and (2) seawater pH. Low nutrient conditions coincide with high abundances of strongly calcified taxa in the Tithonian, whilst high nutrient levels are presumed for the Valanginian. In addition, low pH levels induced by high atmospheric pCO₂ is believed to reduce the calcification rates of modern coccolithophores.

PP41C MCC: Level 2 Thursday 0830h

Nature and Causes of Cyclicity in Triassic Through Miocene

Paleoclimate Records I Posters (*joint with OS*)

Presiding: K L Bice, Woods Hole

Oceanographic Institution; T Wagner, University Bremen

PP41C-0845 0830h POSTER

Seasonal Wildfires as a Mechanism for Long-distance Transportation of Leaf Waxes and Pyrolytic Hydrocarbons in the Aptian-Albian Scisti a Fucoidi, Italian Apennines

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The Scisti a Fucoidi is a heterogeneous pelagic deposit including thinly laminated black shales deposited under poorly- to moderately oxygenated conditions. Black shale deposition was coupled to Milankovitch climatic cyclicity with individual black shales occurring at ~20,000 year intervals. Scisti black shales are characterized by relatively low organic carbon contents (0.41 - 5.69 wt. %) and low Tmax values (411 - 432°C). These strata are at a remarkably low level of thermal maturity as evidenced by the presence of β,β -hopanes. Despite a scarcity of woody or structured terrestrial organic matter, hydrogen indices are low and long-chain n-alkanes show a strong odd/even carbon preference. Consequently, terrestrial organic matter is inferred to derive from input of leaf waxes associated with eolian dust, strong winds and an arid climate on the up-wind landmass. It is notable that Scisti black shales contain greater relative abundances of aromatic hydrocarbons than saturated hydrocarbons. Aromatic hydrocarbons are characterized by a complex mixture of diagenetic and pyrolytic polycyclic aromatic hydrocarbons (PAH). Diagenetic PAH include methylphenanthrenes and chrysene; pyrolytic PAH include phenanthrene, anthracene, fluoranthene, pyrene, benzo[fluoranthene, benzo[ghi]perylene, and coronene. These PAH are inferred to be products of wildfires associated with dry continental conditions, enhancing long-distance transport of pyrolytic PAH. An abundance of pyrolytic PAH in ancient pelagic marine sediments substantiates the linkage between natural burning, atmospheric input and transport of terrestrial organic matter to distal marine basin sites. Winds associated with arid conditions and/or wildfires provide an ideal mechanism for air transport of leaf waxes and pyrolytic PAH to marine sediments. The relative abundance of leaf wax aerosols suggests that there was enough vegetation to generate these waxes and to act as fuel for fires. If landscape denudation occurred following wildfires then nutrient loads to coastal marine settings may have increased resulting in enhanced marine productivity in localized areas.

PP41C-0846 0830h POSTER

Late Cretaceous Layered Cherts in the Pacific Analyzed Using Downhole FMS Logs

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ODP and DSDP drilling of sediments that contain chert has yielded only limited core recovery. The low core recovery results from the contrast in hardness between the chert and the host sediment (often ooze or chalk), because coring is optimized for either hard or soft sediments. During ODP Leg 198 to Shatsky Rise, Hole 1207B was logged using downhole geophysical tools, including the Formation Micro-Scanner (FMS), providing an alternative method of investigating such sequences. The FMS gives a resistivity image of the

borehole wall with a resolution of about 1 cm, and the chert layers stand out as resistive bands in the image. At this site, the chert layers occur on average every 83 cm, with an average thickness of about 9 cm. The cherts are typically layered rather than nodular, suggesting that they formed at horizons that were originally rich in silica, and that diagenesis enhanced this depositional signal. The FMS image logs cover the Cenomanian to Campanian, and the chert layers are most abundant in the Turonian. When the time intervals between chert layers are plotted as a histogram, the intervals cluster around the Milankovitch astronomical periods. Spectral analysis of the FMS data gives peaks in the general range of the astronomical frequencies. We will discuss the various paleoceanographic conditions that could have led to the observed short and long term patterns of chert formation.

PP41C-0847 0830h POSTER

Non-steady state redox conditions in bottom and pore waters of the Mid-Cretaceous NW-African shelf at Tarfaya (SW-Morocco): Climate control and implications for synchrony of basin-wide oxidation of shallow waters during the CT-OAE2

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Widespread deposition of organic-carbon-rich marine sediments during the Oceanic Anoxic Events (OAEs) is a distinct feature of the Cretaceous ocean that was intrinsically linked to periods of extreme oxygen-depletion in the water column. High-resolution geochemical and biofacial records from the southern proto-North Atlantic including the NW-African shelf have recently become available indicating that the redox state of the water column was far from stable during the OAE2. Instead it varied between anoxic/euxinic and probably suboxic/oxic conditions on Milankovitch and maybe even shorter time scales. Despite these stimulating implications little is known about the degree of oxygenation of the water column, the dynamics of contrasting redox conditions, and whether oxidation of the water column occurred synchronous on a basin-wide scale, i.e. across the North American and NW-African shelves. We report millennial-scale geochemical records from a bathymetric transect through the Tarfaya Basin in SW-Morocco to address the nature, pacing, and synchrony of shallow marine redox cycles associated with the OAE2. The data propose that reoxidation of the water column repetitively occurred on orbital frequencies, the transition from anoxic to oxic conditions was abrupt and strong enough to result in distinct metal-rich layers (e.g. Mn) in the sedimentary column. The presence of these distinct layers propose non-steady state diagenesis with progressively downward migrating oxidation fronts. As known from more recent geological analogs, short oxic periods during the OAE2 drastically reduced the preservation potential of marine organic matter in the sediment and supported the re-colonization of the sea floor by benthic organisms. Correlation of one distinct and longer-lasting oxygenation event positioned right in the maximum of the CT global carbon isotopic excursion between the Tarfaya Basin and recently published data from the type section of the Western Interior Basin at Pueblo for the first time allow the discussion of basin-wide synchrony of this oxidation event and probable mechanism.

PP41C-0848 0830h POSTER

Model Simulations of Orbitally Forced Terrestrial and Surface Ocean Variability in the Paleogene Greenhouse Climate

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We have performed an extensive suite of slab ocean GCM experiments in order to begin to understand cyclical changes in carbonate content observed in Paleocene and Eocene sediments recovered from Demerara Rise (ODP Leg 207). In the first part of this study, the sensitivity of surface temperature and moisture flux fields will be compared against globally distributed Eocene terrestrial records in order to deter-

mine the degree to which the model's prediction of atmospheric changes compares with cycles in terrestrial paleoclimate records. In addition, model-predicted upper ocean forcing temperature and moisture flux changes will be compared against variations in planktonic foraminiferal oxygen isotope signals in high resolution Paleogene records from the subtropical North Atlantic. Atmospheric model experiments were performed with the GENESIS v. 2.0 model using an early Eocene paleogeographic reconstruction, 1500 ppm CO₂ and solar luminosity reduced by 0.3 percent from the modern. We have seen that the use of general circulation models to reliably define the paleoclimate variations expected on orbital timescales requires model runs with at least 30 years of quasi-steady state output. A high degree of variance in the precipitation field in tropical latitudes and autocorrelation in surface temperature over ocean model cells requires datasets of at least 30 years of output in order to define statistically significant differences between experiments with different specified orbital configurations.

PP41C-0849 0830h POSTER

Seasonal Isotopic Ca, B, O, C and Sr Fractionation in Late Oligocene Oysters (C. Gigantissima)

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Stable isotope compositions preserved in shell calcite may record various aspects of the environment at the time of calcification. Data from natural samples of *C. gigantissima* from the Belgrade Formation, North Carolina 27+1 Ma, suggest that Ca and B isotope fractionation is temperature dependent and is also a function of water composition. Also, Ca and B isotope fractionation seems to be highly species dependent and for paleotemperature reconstruction it is important to study each species in order to elucidate their response to both temperature and paleo environment. These relationships make seasonal variations in shells extremely useful for interpreting the paleoecology of fossil organisms, as isotope fractionation is different in seawater and brackish water (as seen with oxygen isotopes). In this study, Ca, B, C and O isotopic values were measured along a profile perpendicular to skeletal growth increments, known as stable isotope sclerochronology. This method enables to resolve intra-annual differences in stable isotopes. High resolution O and C isotopic profiles show that *C. Gigantissima* formed skeletal growth increments annually at seasonally varying growth rates, with convex and concave bands forming during summer and winter, respectively (Kirby, 2000). Assuming shell growth ceased at 10C, the estimated paleotemperature derived from oxygen isotopes gives a seasonal range of temperature of ca. 15C, with summer temperatures reaching ca. 25C. Samples from winter and summer bands show a small range of total variation in ⁴⁴Ca/⁴⁰Ca of 0.5 permil. The Ca isotope fractionation is positively correlated to temperature with more positive ^δ⁴⁴Ca of ca. -1.43±0.1 permil in the summer and more negative Ca isotopic compositions of ca. 1.93±0.1 permil in the winter. The data imply a temperature dependence that is ca. 0.03 permil per C. This is significantly less than the 0.24 permil per C reported by Naegler et al (2000) for cultured *Globigerina sacculifer*. However, aragonite precipitated in the laboratory at temperatures of 10 and 40C appears to show an even smaller temperature dependence of approximately 0.01 permil per C (Deyhle et al., 2002) to 0.015 permil per C (Gussone et al., 2003). Additional data gained on O, C and B isotopes further confirm that skeletal growth increments in *C. Gigantissima* show an annual variation, with average seasonal changes of 3.2±0.4 permil, 1.1±0.4 permil and 4.3±0.5 permil, respectively. Interestingly, B isotopes which were previously used as paleo-pH proxy, clearly show an intra-annual temperature dependent fractionation of almost 0.3 permil per C, suggesting that B may be a useful paleo-temperature proxy. Likewise ^δ¹³C, B isotopes may also be influenced by the amount of respired CO₂ reaching the site of calcification. 87Sr/⁸⁶Sr isotopic ratios of 0.70809 ± 0.000018 are the same within our analytical uncertainty and thus suggest fully marine conditions with no change in any freshwater input summer to winter. In summary, stable isotope analysis show significant intra-annual changes which are influenced by temperature and possibly other factors. Further studies need to be conducted on Ca and B isotopes to better understand whether temperature is the main fractionation mechanism on a seasonal time scale or if parameters like shell growth rate and other vital effects play also a critical role in isotopic variations.

PP41C-0850 0830h POSTER

A 9 Million Year Long High-Resolution Benthic ^δ¹³C and ^δ¹⁸O Record: Implications for Late Oligocene to Middle Miocene Paleoceanography

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We present a high-resolution (3 ky) stable isotope time series based on benthic foraminifera data collected from ODP site 926 on Ceara Rise in the western equatorial Atlantic. With data from a second Site 929, the combined record continuously spans a period of almost 9 million years (17.8-26.7 Ma). The age model is based on tuning to a new orbital solution (Laskar 2002). This work extends previously published records deeper into the Oligocene and further into the Miocene in an attempt to create a continuous time-series with the resolution to resolve paleoclimatic change on orbital to tectonic time-scales. As observed previously, the long-term ^δ¹³C and ^δ¹⁸O records collected from benthic foraminifera *C. mundulus* display pervasive cyclic responses at all Milankovitch frequencies with power largely concentrated in the obliquity and 400 kyr eccentricity bands. Cross-spectral analysis of these records and orbital curves indicates a high degree of correlation at all primary Milankovitch periods. The extended, spliced record reveals several new features. Over the long-term, the ^δ¹⁸O record now captures the structure of the late Oligocene warming which initiates at roughly 26.5 Ma, and through a series of steps, peaks by 24.5 Ma, before the initiation of cooling at 23.5 Ma. Over the short-term, high frequency ^δ¹³C cycles with amplitudes in excess of 0.5‰/‰ are evident throughout the record. However, the amplitudes are noticeably higher during two periods, 25.9 to 26.7 Ma in the late Oligocene, and 17.9 to 19.5 Ma in the early Miocene, with minimum falling as low as -1.0‰/‰ during the former. The extreme amplitudes of these ^δ¹³C cycles suggest vertical migration of a mixing line between two water masses, Northern and Southern Component water, implying changes in deep water circulation. Carbonate dissolution proxies support this inference.

PP41D MCC: 3004 Thursday 1020h

Rapid Climate Change During the Holocene and Last Glacial II (joint with A, OS, C, GC)

Presiding: C Morrill, National Center for Atmospheric Research; D M Anderson, NOAA Paleoclimatology Program

PP41D-01 1020h

Radiocarbon Record of Rapid Deep Water Production Changes During the Last Deglaciation

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Several dramatic excursions in the oxygen isotope values of Greenland ice cores and corresponding increases in polar sea ice extent occur during the last deglacial interval. The fate of North Atlantic Deep Water (NADW) during these brief excursions is of great interest but is poorly documented due to a lack