

Elevated CO₂ levels in the Peri-Tethys during the Middle Eocene Climatic Optimum

A CO₂ reconstruction using carbon isotope fractionation of organic matter from the Belaya River Section, Russia

Master's Thesis

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Abstract

The Middle Eocene Climatic Optimum (MECO) is a phase of climate warming that occurred ~40 Ma, encountered globally as a negative δ^{18} O excursion. To examine its cause and exceptional duration of 500,000 years, more knowledge on the carbon cycle during the MECO is required. Therefore, this thesis presents a CO₂ reconstruction based on carbon fractionation of bulk organic matter from Eocene shelf sediments deposited in the Peri-Tethys. To test if bulk organic matter primarily represents a marine signal, the BIT index and C:N were applied. A TEX₈₆ temperature reconstruction was performed as sea-surface temperatures must be accounted for when reconstructing CO₂. Finally, carbonate content and total organic carbon were calculated to study environmental effects of the MECO and test if carbonate deposition shifted from the deep ocean to the shelves, as is hypothesized to explain the remarkable duration of the MECO. The position of the MECO was successfully determined using δ^{18} O. It coincides with a distinctive TOC increase and carbonate decrease, possibly due to changes in productivity, oxygen conditions and/or carbonate production. BIT index and C:N indicate negligible to low terrestrial input throughout the section and reconstructed temperatures suprisingly indicate no warming during the MECO. Finally, a CO₂-level increase of at least 50-350 ppmv during the MECO is inferred.

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1. Introduction

A major scientific challenge is understanding the impact of anthropogenic greenhouse gas emissions on Earth's climate. Well informed policy making requires further constrains on factors such as equilibrium climate sensitivity - currently estimated at the broad range of 1.5 to 4.5 °C – and sea level rise (IPCC, 2014). One method to improve our understanding of the climate system is studying past climate changes. These events allow us to examine factors such as the aforementioned climate sensitivity, by reconstructing CO_2 -levels and the accompanying temperatures (Rohling et al., 2012), and ocean acidification, by studying its magnitude and biological effects under different CO_2 -level increases (Hönisch et al., 2012).

Frequently, paleoclimatic studies focus on periods of severe warming that are, to an extent, analogous to current climate change. The Eocene epoch (56.0 - 33.9 Ma) contains several such rapid and relatively short-lived warming events, referred to as hyperthermals, of which the Paleocene-Eocene Thermal Maximum (PETM) is the most notable (Zachos et al., 2008).

A similar Eocene warming event occurred around 40 Ma, interrupting the general middle Eocene cooling trend, known as the Middle Eocene Climatic Optimum (MECO) (Bohaty & Zachos, 2003). Since its discovery in the Southern Ocean, the MECO has been encountered on both hemispheres in high as well as low latitudes (e.g. Jovane et al., 2007; Edgar et al., 2010; Kamikuri et al., 2013; Boscolo Galazzo et al., 2014). It is associated with elevated CO₂ levels and a warming of 4 to 6 °C, with peak MECO sea surface temperatures exceeding 28 °C in the Pacific Ocean (\sim 65°S paleolatitude) (Bijl et al., 2010). The MECO appears to coincide with enhanced biological productivity in ocean surface waters, as has been observed in several records from the Tethys Ocean (Boscolo Galazzo et al., 2013; Savian et al., 2014) and Atlantic Ocean (Boscolo Galazzo et al., 2014; Witkowski et al., 2014; Moebius et al., 2015). Proposed causes include extrusive volcanism in present-day Iran (Van der Boon, 2017) and metamorphic alteration of carbonates as a result of carbonate-rich oceanic plate subduction (Bohaty & Zachos, 2003).

What separates the MECO from most warming events is its duration of approximately 500,000 years. This duration poses a scientific problem, as carbon cycle theory predicts that increased silicate weathering in combination with carbonate deposition should cause CO_2 concentrations to fall to pre-event conditions within approximately 100,000 years, as in the case of the PETM (Sluijs et al., 2013). Model simulations ran by Sluijs et al. (2013) confirm the existence of this problem, finding only one scenario explaining the exceptionally long duration of the MECO: a rising sea level causing weathering rates to decrease on the drowned continental shelves and a carbonate burial shift from the deep ocean to continental shelves.

The first observations needed to test this hypothesis have since been made, such as $^{187}Os/^{188}Os$ measurements that indicate no substantial increase in silicate weathering during the MECO (Van der Ploeg, in review). As stated by Sluijs et al. (2013), to further test the hypothesis, additional assessment is needed of the precise timing of temperature changes on different latitudes, sea level changes and the evolution of the carbon cycle, particularly carbonate dissolution, ocean alkalinity and pCO₂.

So far, a CO₂ increase during the MECO has only been demonstrated by Bijl et al. (2010). They inferred pCO₂ using the carbon isotopic composition of diunsaturated alkenones. However, the resolution of their record is limited, with less than ten data points in the time span of the MECO, and the uncertainties are in the order of thousands of ppmv as a result of low alkenone concentrations. Although an apparently continuous CO₂ release throughout the MECO is inferred, a more detailed view is needed to enhance our understanding of the magnitude of CO₂-level increase, its termination and the cause of the MECO (Sluijs et al., 2013). To this end, a CO₂ reconstruction with a higher resolution is attempted in this thesis, by applying carbon isotope fractionation of bulk organic material in Peri-Tethys shelf sediments sampled at the Belaya River Section, Russia. This section provides an apparently continuous succession of carbonate- and organic matter-rich sediments from the middle Eocene to the Oligocene and offers a perspective on environmental changes on the

continental shelf rather than the deep ocean, providing a test of the hypothesis that carbonate deposition shifted to the shelves (Van der Boon, 2017).

The foundation of the CO_2 -reconstruction method is the discrimination of carbon-fixing enzyme ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCO) against heavier ¹³C isotopes in favour of the lighter ¹²C, causing marine primary producers to fractionate carbon isotopes during photosynthesis. This fractionation effect is amplified under higher CO_2 concentrations, implying carbon isotope fractionation of organic matter relative to the carbon isotope ratio of dissolved inorganic carbon may provide an indication for the CO_2 concentrations in which this organic matter is produced (Popp et al., 1989; Popp et al., 1998; Burkhardt et al., 1999).

In practice, this principle is indeed applied to reconstruct CO₂ concentrations, often using the δ^{13} C of specific organic compounds associated with marine primary producers , most commonly diunsaturated alkenones (e.g. Pagani, 2002; Pagani, 2005; Bijl et al., 2010), but also porphyrins (e.g. Freeman & Hayes, 1992) and phytane (e.g. Bice et al., 2006), among others. This is necessary because bulk organic matter does not exclusively contain primarily produced material and because terrestrial organic material in marine sediments, derived from plant remains and pollen, alters organic δ^{13} C, affecting CO₂ concentrations calculated (Pagani et al., 2000; Sluijs & Dickens, 2012).

However, Naafs et al. (2016) showed that executing such a CO₂ reconstruction for Oceanic Anoxic Event II using pristane, phytane, C₁₇N-alkane and C₁₈-alkane yielded similar results as using bulk organic material, because the bulk organic matter measured was dominated by marine material, rendering the measurement of separate components specific for marine primary producers less necessary. This indicates that if organic matter is either dominantly marine or the influx of terrestrial material can be corrected for, δ^{13} C of bulk organic matter ($\delta^{13}C_{org}$) may be applicable to determine carbon fractionation by marine primary producers and can therefore serve as a CO₂ proxy, inferring the isotopic composition of water from bulk carbonate δ^{13} C ($\delta^{13}C_{carb}$). This suggests CO₂ reconstructions may also be possible when the use of organic molecules such as alkenones is not possible.

To test whether this applies to the studied marine sediments, terrestrial input can be estimated by applying the BIT index, which describes the relative contribution of marine and terrestrial types of GDGTs. According to Hopmans et al. (2004), the BIT index appears to be applicable to reconstruct the input of terrestrial organic matter in marine sediments at least up to the Cretaceous and it has been successfully applied on Eocene sediments before (Sluijs et al., 2011; Sluijs & Dickens, 2012). Additionally, C:N ratios are applicable, as they provide an estimate of terrestrial input because of the absence of cellulose in algae and its abundance in vascular plants, giving each group distinct C:N ratios. In spite of diagenetic alterations, the relative signal appears to be retained in organic material for millions of years, although diagenesis may impact the absolute ratios (Meyers, 1994).

As temperature impacts algal fractionation, temperature estimates are required to calculate CO_2 concentrations from $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$. Therefore, a temperature reconstruction based on TEX₈₆ (short for tetraether index of 86 carbon atoms) is presented in this thesis. This paleothermometer is based on the correlation between sea-surface temperature (SST) and the relative abundance of different ring-containing glycerol dialkyl glycerol tetra-ethers (GDGTs), membrane lipids produced by marine Thaumarchaeota (Schouten et al., 2002).

Additionally, this thesis contains an assessment of carbonate content and total organic carbon (TOC), to see whether the shift in carbonate deposition from deep waters to the shelf suggested by Sluijs et al. (2013) can be validated and to examine possible environmental shifts.

2. Materials and methods

2.1 Sample collection and geological setting

2.1.1 Sample collection

Conventional paleomagnetic cores were taken over an estimated stratigraphic depth of 28.7 m using a gasoline-powered hand drill at the Belaya River Section in August 2017. This section is situated approximately 30 km south of the town Maikop in the Crimea-Caucasus region, Russia (Figure 1). The overall average sample spacing of the studied stratigraphy is 19 cm, average sample size around the position of the MECO (1100-1900 cm) is 10 cm.

2.1.2 Basinal setting

The Belaya River Section is located on the edge of the Scythian Platform and the Greater Caucasus mountain range. The sampled sediments of Eocene age were deposited in the north-eastern Peri-Tethys, the epicontinental part of the gradually closing Tethys Ocean, which covered large parts of present-day southern Asia (Akhmetiev et al., 2012; Benyamovskiy, 2012; Van der Boon, 2017). The Peri-Tethys was part of a large shelf ocean dominated by biogenic deposits (Radionova et al., 2003). The basin is believed to have been open until the Oligocene, when it transitioned into a partially enclosed basin with dysoxic-anoxic conditions prevailing for over 15 My. From this partial enclosing event onwards, the Peri-Tethys is referred to as Paratethys (Van der Boon, 2017).



Figure 1: Map of Eastern Europe/Western Asia, indicating the sample location at the Belaya River in south-eastern Russia with a yellow arrow (modified after Google Maps). In the Eocene, this location was part of the epicontinental Peri-Tethys.

2.1.3 Stratigraphic succession

The section presented in this thesis contains approximately 30 m of the ~57 m thick Kuma formation (see Figure 2), which consists of laminated (millimetre scale), organic rich marls of brownish colour. As a result of weak magnetic signals and a lack of nannoplankton and dinoflagellate biomarker species within the Kuma formation, no detailed age model has been constructed so far, but it has been established that a large part of the Kuma formation is of Bartonian age (41.2 - 37.8 Ma) (Van der Boon, 2017)(Van der Boon, 2017). In the lower part, the Kuma formation contains several bentonite layers; in the middle part, alternations between lighter marls of ~0.5 m and darker marls of 3-5 cm are observed; in the upper part, plant debris is found (Benyamovskiy, 2012). Pyrite nodules are present at the base and top. Fish remains are abundant and generally little bioturbation is observed (Van der Boon, 2017). Based on its high organic carbon content and benthic

foraminifera assemblages, the Kuma formation is interpreted to be deposited in relatively oxygen-depleted conditions, including several episodes of dysoxic to anoxic conditions (Gavrilov et al., 2000; Benyamovski et al., 2003).

Despite the sharp shift in lithology and faunal assemblage, the contact between the Kuma formation and the underlying Cherkessk formation (Ypresian-Lutetian Age) is interpreted to be conformable. Therefore, the boundary is considered to represent a rapid environmental shift, possibly a result of ocean cooling (Benyamovski et al., 2003; Radionova et al., 2003).

The Kuma formation transitions into the Maikop series, which consists of dark, organic-rich clays and contains an ash layer whose biotite crystals were Ar-Ar dated, yielding an absolute age of 33.2 \pm 0.34 Ma (2 σ), close to the Eocene-Oligocene transition (Van der Boon, 2017b).

2.2 Stable isotope and sediment composition measurements

2.2.1 Bulk carbonate isotope measurements

To prepare samples for bulk carbonate isotope measurements (δ^{13} C and δ^{18} O), ~10 g of sediment per sample was freeze dried, scraped clean and crushed into powder. The carbonate fraction of the resulting bulk material was measured with a Thermo Finnigan GasBench-II carbonate preparation device coupled to



Figure 2: Log of the sampled Belaya River Section containing formations and formations boundaries (modified after Morton, M., unpublished). The black bar denotes the part of the section discussed in this thesis.

a Thermo Finnigan Delta-V isotope ratio mass spectrometer (IRMS), aiming for 50-100 µg of carbonate per measurement. On every 79 measurements, 9 naxos standards were measured for analytical corrections as well as 4 IAEA-CO-1 standards to calculate analytical error. Analytical errors are estimated to be ~0.1‰ for δ^{13} C and δ^{18} O. δ^{13} C and δ^{18} O values reported are relative to the Vienna Pee Dee Belemnite (VPDB) standard.

2.2.2 Organic carbon isotope and carbonate content measurements

To prepare the carbon isotope measurements on the organic carbon fraction, 0.2-0.3 g of the bulk material of each sample was decalcified following established protocols. Samples were transferred to Greiner tubes and decalcified by adding 7.5 ml HCl, shaking the tubes (110 times per minute) for 4 hours, centrifuging and decanting. These steps were repeated a second time, with the tubes being shaken for approximately 16 hours. Two times, the samples were washed by adding 10 ml of de-ionized water, centrifuged and decanted. These cleaned samples were dried in an oven at 60 °C for 72 hours. Carbonate content of each sample was approximated by using the mass difference between the decalcified sediment and the original sediment.

After crushing the decalcified material, it was placed in tin cups, aiming for 10-40 μ g of organic material per sample. $\delta^{13}C_{org}$, organic carbon content and organic nitrogen content were measured using a Thermo Scientific Flask 2000 elemental analyzer coupled to a Thermo Scientific Delta V Advantage via a Conflo IV Elemental Analyser-Isotope Ratio Mass Spectrometer (EA-IRMS). On every 96 measurements, 17 GQ standards were measured for analytical corrections, 8 nicotinamide standards to calculate analytical error, TOC and C:N, and 3 blanks to correct for carbon contained in the tin cups. Analytical errors are estimated to be ~0.1‰ for $\delta^{13}C_{org}$. $\delta^{13}C$ values reported are relative to the Vienna Pee Dee Belemnite (VPDB) standard.

2.2.3 Total organic carbon and C:N determination

To calculate total organic carbon content from EA-IRMS results, the amount of organic carbon per peak area was determined using nicotinamide, a standard with a fixed carbon percentage of 59.01%. For every sample, the total amount of measured organic carbon was calculated, correcting for the average peak area of the blank cups. Dividing this by the total amount of weighed sample yields the percentage of organic carbon in decalcified material. After correcting for the carbonate fraction determined during decalcification, the total organic carbon percentage of the bulk rock was found. The same procedure was used to calculated total organic nitrogen (nicotinamide having a nitrogen percentage of 22.94%). Dividing the percentage of carbon by the percentage of nitrogen yields the C:N ratio.

2.3 Lipid extraction

Lipids were extracted from approximately 10 grams of crushed bulk sediment sample with a Accelerated Solvent Extraction (ASE) machine, using dichloromethane:methanol (9:1) as solvent and diatom earth as extraction-enhancing, porous medium. The same was done for a blank and a diatom-earth blank, to check for methodological contamination. The resulting total-lipid extracts were concentrated, transported to previously weighed glass vials and evaporated.

Apolar-, ketone- and polar-lipid fractions were separated using small column chromatography, with activated aluminiumoxide as medium. After cleaning the column with hexane:dichloromethane (9:1), the same solvent was used to separate the apolar-lipid fraction, followed by hexane:dichloromethane (1:1) for the ketone fraction, and finally dichloromethane: methanol (1:1) for the polar fraction. A C_{46} standard of 198 ng was added to the polar fraction to be able to calculate absolute GDGT-abundances. All solutions were collected in glass vials and dried under nitrogen flow. The dried polar-lipid fractions were dissolved in hexane: isopropyl alcohol (99:1), filtered using a filter syringe and diluted to approximately 2 mg/ml using the same solvent.

GDGT measurements were performed using High Performance-Liquid Chromatography-Mass Spectrometry (HP-LC-MS) with an Agilent 1260 UHPLC coupled to a 6130 quadrupole MSD as described by Hopmans et al. (2016). Two Ultra High Performance-Liquid Chromatography (UHPLC) silica columns combined with a 2.1 x 5 mm silica pre-column were applied to separate fractions in approximately 5 μ l of sample, at a constant 30 °C. Elution of GDGTs was performed with a mobile phase composition of 18% hexane:isopropanol (9:1) relative to hexane for 25 minutes, linearly increasing to 35% in the following 25 minutes, finally linearly increasing to 100% in 30 minutes with a flow rate of 0.2 ml/min and a maximum back pressure of 230 bar. Run time was 90 minutes, reequilibration time 20 minutes.

To test for the presence of alkenones, pristine and phytane, two ketone fractions and two apolar fractions from the same sample (stratigraphic positions of 1215 and 1470 cm) were dissolved in 50 ml and 100 ml of hexane, respectively, and measured with a Hewlett Packard gas chromatograph fitted with a flame ionization detector chromatographer following the method described by Speelman et al. (2009). Samples were injected on-column on a CP-Sil 5CB fused silica column of 30 m x 0.32 mm and a film thickness of 0.1 μ m, with helium as carrier gas kept at a constant pressure of 100 KPa. The temperature was 70 °C during injection, increasing with 20 °C/min to 130 °C, then increasing with 4 °C/min to 320 °C, which was maintained for 20 minutes. Component identification was performed with GC/MA (Thermo Trace GC Ultra) with the same protocol.

2.4 TEX₈₆

2.4.1 Temperature reconstruction

The different GDGT peaks retrieved by the HP-LC-MS were integrated to retrieve the relative abundance of different GDGTs following Schouten et al. (2007). Using the following formula, relative GDGT abundances were converted to TEX₈₆ values.

$$TEX_{86} = \frac{[GDGT - 2] + [GDGT - 3] + [Cren']}{[GDGT - 1] + [GDGT - 2] + [GDGT - 3] + [Cren']}$$

The logarithmic calibration by Kim et al. (2010) was applied to convert TEX₈₆ into temperature, as this is most suitable for the high Eocene temperatures:

$$SST = 68.4 \cdot \log(TEX_{86}) + 38.6$$

2.4.2 TEX₈₆ bias controls

Under certain conditions, microbes may GDGTs that do not follow the temperature calibration, thereby altering TEX_{86} and leading to incorrect temperature reconstructions. Several such processes are reflected in the ratio of different GDGTs and can therefore be detected.

The methane index (MI) as developed by Zhang et al. (2011) was applied to detect whether methanotrophic archaea significantly contributed to the GDGT distributions. Values >0.5 are suspicious.

$$MI = \frac{[GDGT - 1] + [GDGT - 2] + [GDGT - 3]}{[GDGT - 1] + [GDGT - 2] + [GDGT - 3] + [Crenarchaeol] + [Cren']}$$

Similarly, if the relative occurrence of GDGT-0 compared to crenarchaeol is more than 67%, this indicates substantial input of methanogenic GDGTs (Blaga et al., 2009; Sinninghe Damsté et al., 2012).

The ring index (RI), representing the average ring number on the measured GDGTs, indicates whether non-thermal factors, such as nutrient availability, have influenced TEX_{86} when RI deviates from the common correlation found with TEX_{86} too strongly (Zhang et al., 2016).

$$RI = 0 \cdot [GDGT - 0] + 1 \cdot [GDGT - 1] + 2 \cdot [GDGT - 2] + 3 \cdot [GDGT - 3] + 4 \cdot [Crenarchaeol] + 4 \cdot [Cren']$$

Furthermore, GDGT synthesis by Euryarchaeota performing anaerobic methane oxidation in the sulphate-methane transition zone (SMTZ) was checked using the ratio between GDGT-2 and Crenarchaeol, which yields an average ratio of 0.3 for GDGTs produced outside of the SMTZ and 0.18 for GDGTs inside the SMTZ (Weijers et al., 2011). Ratios of GDGT-2/GDGT-3 higher than 5 indicate whether deep-water GDGT production impacts TEX₈₆ (Taylor et al. 2013; Hernández-Sánchez et al., 2014).

Finally, the branched and isoprenoid tetraether (BIT) index indicates to what extent the sample has been contaminated with terrestrially derived GDGTs, either during original deposition or during sample collection. It describes the relative contribution of marine and terrestrial types of membrane lipids known as glycerol dialkyl glycerol tetra-ethers (GDGTs). A BIT index of 0 indicates no GDGTs of terrestrial origin, while a BIT index of 1 indicates all GDGTs are terrestrially derived.

$$BIT = \frac{[I + II + III]}{[I + II + III + IV]}$$

I, II and III = branched GDGTs (brGDGTs), primarily produced by terrestrial soil microbes IV = isoprenoid GDGT, >99% produced by marine crenarchaeota (Hopmans et al., 2004)

2.5 CO₂ reconstruction

To estimate CO_2 concentrations from carbonate and organic carbon isotope compositions, fractionation (ϵ_p) and dissolved CO_2 ($CO_{2(aq)}$) were calculated following the method by Pagani et al. (2005).

 ϵ_p , a factor representing carbon isotopic fractionation by primary producers during photosynthesis, depends on the isotopic difference between dissolved CO₂ and primarily produced marine organic material.

$$\varepsilon_p = \left[\frac{\delta^{13} C_{(aq)} + 1000}{\delta^{13} C_{org} + 1000} - 1 \right] * 1000$$

 $\delta^{13}C_{(aq)}$ = isotopic composition of dissolved CO₂ $\delta^{13}C_{org}$ = isotopic composition of primarily-produced marine organic material (Freeman & Hayes, 1992)

 $\delta^{13}C_{(aq)}$ differs from $\delta^{13}C_{carb}$ due to a carbon-precipitation enrichment effect (Romanek et al., 1992) and an additional temperature dependent fractionation between dissolved CO₂ and HCO₃⁻ (Mook et al., 1974). To correct for this, the fractionation factor of bulk carbonate ($\delta^{13}C_{calc}$) to gaseous CO₂ (CO_{2(g)}) and the fractionation factor of gaseous CO₂ (CO_{2(g)}) to dissolved CO₂ (CO_{2(aq)}) are required.

$$\varepsilon_{calc-CO_2(g)} = 11.98 (\pm 0.13) - (0.12(\pm 0.01) * T)$$

(Romanek et al., 1992)

$$\varepsilon_{CO_2(g)-CO_2(aq)} = \frac{-373}{273.15+T} + 0.19$$

(Mook et al., 1974)

Temperatures (T) were interpolated linearly between data points. Using these fractionation factors, first $CO_{2(g)}$ and finally $CO_{2(aq)}$ can be calculated.

$$\delta^{13}C_{CO_2}(g) = \frac{\delta^{13}C_{calc} + 1000}{1 + \varepsilon_{calc} - CO_2(g) * 0.001} - 1000$$

$$\delta^{13}C_{(aq)} = ((0.001 * \varepsilon CO_2(g) - CO2(aq) + 1) * (\delta^{13}CCO_2(g) + 1000)) - 1000$$

With ε_p , dissolved CO₂ concentrations [CO_{2(aq)}] can be estimated. When assuming that CO₂ enters the cell via passive diffusion, [CO_{2(aq)}] is described as:

$$[CO_{2(aq)}] = \frac{-b}{\varepsilon_p - \varepsilon_f}$$

 ε_f = Maximum isotopic fractionation of RuBisCO, conservatively estimated at 25-28‰ for marine algae with C₃-type metabolisms (Pagani, 2002)

b = Combined species-specific factors reflecting physiological factors (e.g. growth rate and cell geometry)

(Popp et al., 1989; Popp et al., 1998)

The *b*-value can either be estimated using $\delta^{15}N$, as this supposedly scales linearly with *b* (Andersen et al., 1999), or using $[PO_4^{3-}]$, to which the *b*-value correlates in modern oceans (Pagani et al., 2005). Neither $\delta^{15}N$ nor $[PO_4^{3-}]$ data was available to constrain the *b*-value, so a wide range of 100 to 200 was used, which is broadly the range encountered in modern oceans (Bidigare et al., 1999).

With $[CO_{2(aq)}]$ estimated, pCO₂ can be calculated using Henry's Law, assuming ocean surface water and the atmosphere to be in equilibrium:

$$pCO_2(ppmv) = \frac{[CO_2(aq)]}{K_0}$$

K₀ = Solubility constant, depending on salinity and temperature:

$$ln K_0 (moles/l \cdot atm) = A_1 + A_2 \frac{100}{T} + A_3 ln \frac{T}{100} + S \left[B_1 + B_2 \frac{T}{100} + B_3 \left(\frac{T}{100} \right)^2 \right]$$

T = Temperature (K) S = Salinity (‰) $A_1 = -58.0931$ (moles/l·atm) $A_2 = 90.5069$ (moles/l·atm) $A_3 = 22.2940$ (moles/l·atm) $B_1 = 0.027766$ (moles/l·atm) $B_2 = -0.025888$ (moles/l·atm) $B_3 = 0.0050578$ (moles/l·atm) (Weiss, 1974)

3. Results

3.1 Stable isotope ratios and fractionation

Bulk sediment $\delta^{18}O_{carb}$ shows a distinct negative excursion, from an average of -4 to a minimum of -6‰, between 1200 and 1600 cm, with a gradual decrease starting at about 1000 cm (Figure 3). Average error margin for $\delta^{18}O$ is 0.108‰. A positive $\delta^{13}C_{carb}$ excursion is observed in the same interval, with values increasing from approximately 1.5‰ to values over 2‰. Average error margin for $\delta^{13}C_{org}$ varies between approximately -27.5 and -26.5‰, with a nearly instantaneous shift at 1500 cm towards heavier values of -26 to -25.5‰, followed by a gradual recovery. Around 1400 cm, right before this shift, a small negative excursion appears to be distinguishable. Average error margin for $\delta^{13}C_{org}$ is 0.109‰, with a relatively high error margin of 0.161‰ for part of the measurements, possibly the result of analytical instability or pollution (see Appendix 3 for a more detailed view of error margins).



Figure 3: Bulk carbonate and organic carbon isotope data in the Belaya River Section: $\delta^{18}O_{carb}$, $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$. The first sedimentological log indicates grain sizes, the second log indicates rock colour. Circles indicate individual measurements, solid lines indicate five-point moving averages (not extended to the beginning of the succession for $\delta^{18}O_{carb}$ due to resolution gaps). A distinct negative oxygen isotope excursion of 2‰ is interpreted to represent the MECO (see Discussion, section 6.1), indicated by the yellow shaded area. In approximately the same interval, a positive carbon-isotope excursion is observed. A positive organic carbon isotope shift occurs during the termination of the MECO. A selection of error bars is presented (see Appendices 1-3 all errors), representing analytical error (1 standard deviation of measured IAEA-CO-1 and nicotinamide for bulk carbonate and bulk organic data, respectively). As an age model is absent, data is plotted in the depth domain.

3.2 Sedimentary composition and terrestrial input indicators

Carbonate content is relatively high, varying between approximately 55% and 80% throughout the section, with distinctly lower concentrations up to 33% between 1300 and 1600 cm (Figure 4). In the same interval, TOC increases from 2-3% to 5% and higher. The organic carbon content in decalcified sediment, representing the fraction of organic carbon compared to siliciclastic material such as silt and clay, shows no trend break in same interval.

Up to 1000 cm, C:N generally ranges from 14-20 (Figure 4). Between 1000 and 1500 cm, the ratio gradually increases, going up to 18-23, after which C:N remains stable. The BIT index varies between 0.00 and 0.03, indicating negligible to no input of soil GDGTs throughout the section.



Figure 4: Sediment composition in the Belaya River Section: carbonate content, TOC, organic C in decalcified material, and C:N. A rapid decrease in carbonate content and a TOC increase occur simultaneously during the MECO, while the concentration of organic carbon in decalcified material, representing the proportion of organic matter compared to terrestrial material, shows little to no change. A slight C:N increase is observable from approximately 1000 to 1500 cm, after which the ratio remains stable. Carbonate content shows total percentage of weight lost during decalcification as maximum (left) and 80% of weight lost as minimum (right), accounting for the potential dissolution of minerals other than calcium carbonate. The purple line in the C:N graph represents the 5-point moving average. Error ranges surrounding TOC and organic C in decalcified material are based on the standard deviation found in nicotinamide, applied as a percentage instead of an absolute value because of large organic-content differences between nicotinamide and samples. The yellow shaded area indicates the position of the MECO. As an age model is absent, data is plotted in the depth domain.

3.3 Biomarkers and temperature reconstruction

Alkenones are not present in two tested samples, which are situated prior to and inside the MECO interval at 1215 and 1470 cm, respectively. Phytane and pristane do appear to be present in these samples. GDGT concentrations are sufficient for accurate measurements in all tested samples (see Appendix 3). The BIT index varies between 0 and 0.03, indicating little to no contamination from soil-derived GDGTs. The results of 5 of the 20 samples were successfully duplicated. The amount of GDGTs present in both the blank sample and the diatom-earth sample are negligible. The methane index, ring index, and %GDGT-0 vs. Crenachaeol do not indicate alternative processes disturbing the temperature signal. In ten samples, GDGT-2/GDGT is \geq 4.5, approaching the suspicious value of 5, and surpasses this value once, reaching 5.6 in the sample at 2600 cm. GDGT-2/Crenachaeol ranges from 0.11 – 0.15, which is relatively close to the 0.18, the average ratio found in GDGTs formed in the modern-day SMTZ.

TEX₈₆ indicates no warming took place on the sampled location during the MECO. Instead, it suggests a gradual cooling during this period, with temperatures decreasing from 33-34 °C to 31-32 °C over the course of the section. The data point at 2600 cm and 900 cm stand out as outliers with respect to this trend.



surface Figure 5: Sea temperatures based on the TEX₈₆ paleothermometer and carbon isotope fractionation (ε_p) derived from the Belaya River Section. SST and fractionation are shown with three-point and fivepoint moving averages, yellow respectively. The shaded area indicates the position of the MECO. No temperature increase is observable during the MECO. Instead, а slight cooling appears to overlap with the event. There appears to be a cooling trend throughout the section. Error bars of TEX₈₆ are based on analytical error and the calibration error as denoted by Kim et al. (2010).

3.4 Fractionation

Carbon isotope fractionation (ϵ_p) of organic matter relative to bulk carbonate (here used as a proxy for dissolved inorganic carbon in sea water) is around 20‰, with an increase to approximately 21‰ coinciding with the oxygen isotope excursion.

4. Discussion

4.1 Isotope stratigraphy and fractionation

The distinct negative oxygen isotope excursion between 1200 and 1600 cm may represent the MECO, which is expressed as an oxygen-isotope excursion globally (e.g. Bohaty & Zachos, 2003; Bijl et al., 2010; Galazzo et al., 2014). The Kuma formation is mainly of Bartonian age (41.2-37.8 Ma) and the excursion is similar in shape as the MECO excursion on other locations (e.g. Bohaty et al., 2009; Spofforth et al., 2010). Furthermore, like in other Tethys sections, the peak is associated with a decrease in carbonate content of about 20% (e.g. Jovane et al., 2007; Spofforth et al., 2010).

The magnitude of $\delta^{13}C_{carb}$ is comparable to values from other Bartonian sedimentary successions and the observed positive excursion may correspond to a positive excursion associated with the MECO in records worldwide, including several from the Tethys Ocean (Bohaty et al., 2009; Spofforth et al., 2010). In many other records, one or several negative carbon isotope excursions are also observed before, during and after the MECO in carbonates. Spofforth et al. (2010) recognized three such negative carbon isotope excursions, two right before and one right after the positive excursion, in locations around the globe, including in the western Tethys. These are not discernible in the record presented here. Notably, another Tethys section from the Apennines, Italy, also contains a

distinct positive excursion without clear negative excursions, akin to the Belaya record (Jovane et al., 2007). Furthermore, the records presented by Spofforth et al. (2010) and Bohaty et al. (2009) show large variations in the distinctness of both negative and positive δ^{13} C excursions, with truly distinct negative excursions found primarily in the Southern Hemisphere. Therefore, it appears that the occurrence of carbon isotope excursions is inconsistent among locations and that the negative carbon isotope excursion may not be as closely associated with the MECO as previously reported. Potential causes for the observed differences include spatial differences in organic carbon burial, primary productivity and local negative carbon sources such as methane hydrates (Ripperdan, 2001). Missing excursion may also be partially explained by resolution issues, causing smaller excursions to be missed.

The δ^{18} O values of -4 to -6‰ are strikingly negative compared to the values of ~0‰ in other isotope records of middle Eocene age, including those based on bulk carbonate instead of foraminifera (e.g. Bohaty et al., 2009; Bijl et al., 2010; Boscolo Galazzo et al., 2014). Instead, these negative values are closer to the isotopic composition of meteoric waters, suggesting the negative values might be the result of diagenetic reactions with groundwater (Gat, 1996). This implies that if the oxygen isotope excursion includes a temperature signal, it cannot be used to quantitatively derive temperature changes and should only serve as a chemostratigraphic marker for the MECO.

It also suggests that the excursion may represent a diagenetic overprint resulting, likely from differences in carbonate content or TOC rather than a temperature signal, as the isotopic changes coincide with these sedimentological changes. When plotting δ^{18} O against carbonate content, a relationship indeed appears to exist (Figure 6). However, it cannot be excluded that this relationship exists because carbonate deposition is coupled to climatic conditions represented by δ^{18} O, with the climate change causing changes in sediment composition (see Discussion, section 4.2).

Diagenetic alteration may explain why in more western sections of the Tethys, the first half of the MECO is found below two TOC-rich layers (Spofforth et al., 2010; Boscolo Galazzo et al., 2013), while in this study, the MECO as a whole would be present within a TOC-rich layer. However, in the Tethys section studied by Jovane et al. (2007), the MECO is also found inside a TOC-rich layer and not partially underneath it, meaning these lithological differences may be attributed to regional environmental differences.

A scenario of diagenetic alteration is complicated by the fact that $\delta^{13}C_{carb}$ shows an excursion in the expected MECO interval and, subsequently, ε_p increases, indicating elevated CO₂ levels (see Discussion, section 4.5). This can only be explained by diagenesis if $\delta^{13}C_{carb}$ is altered by a similar process as $\delta^{18}O$, but when plotting $\delta^{13}C_{carb}$ against $\delta^{18}O$ or carbonate, no clear connection appears (Figure 6). Furthermore, $\delta^{13}C$ values differ vastly from those found in ground water, which are -10‰ or more negative, with typical values for precipitated carbonate being -25‰ (Rightmire & Hanshaw, 1973). Instead of moving towards these more negative values, as would be expected with enhanced diagenetic alteration, $\delta^{13}C_{carb}$ becomes more positive. Therefore, it appears unlikely that $\delta^{13}C_{carb}$ underwent a similar diagetic alteration as $\delta^{18}O$, implying it represents an environmental signal. Microscopically studying bulk carbonate or foraminific samples might provide additional information on whether the samples underwent severe diagenesis.

As an accurate age model is currently not available, the excursion cannot be dated exactly and certainty about it coinciding with the MECO cannot yet be given. However, considering that the MECO has so far been recorded worldwide, including in Tethys sediments (Spofforth et al., 2010), and a positive $\delta^{13}C_{carb}$ excursion and ϵ_{p} -increase coincide with the interval, the oxygen isotope excursion is interpreted to represent the MECO.



Figure 6: Isotope data plotted against other data. The upper-left graph shows δ^{18} O plotted against carbonate content, the upper-right graph shows $\delta^{13}C_{carb}$ plotted against carbonate content, the lower-left graph sows δ^{18} O plotted against $\delta^{13}C_{carb}$ and the lower-right graph shows $\delta^{13}C_{org}$ plotted against TOC. The red lines denote a linear fit. R², an indication of how close this fit is, with 0 being no fit and 1 a perfect fit, is provided.

4.2 Environmental shifts during the MECO

The δ^{18} O peak interpreted to represent the MECO coincides with a marked increase in TOC and decrease in carbonate content. These observations can either be explained by an increase in organic matter deposition, a decrease in carbonate deposition, or a combination. Considering that an organic carbon increase is not discernible when looking at carbon concentrations relative to detritic material, increased deposition of organic matter can only be an explanation if deposition of the remaining fraction, mainly silt and clay, experienced the same relative deposition increase.

4.2.1 Enhanced organic matter deposition scenarios

The first scenario explaining the observations is enhanced primary production at the ocean surface combined with increased terrestrial sediment deposition by rivers or wind. Indications for enhanced sea-surface primary production during the MECO have been found in the western Tethys (Toffanin et al., 2011; Boscolo Galazzo et al., 2013; Savian et al., 2014), the western North Atlantic (Witkowski et al., 2014) and the subtropical North Atlantic (Moebius et al., 2015). Savian et al. (2014) found evidence for enhanced detrital mineral input as well, which they attributed to an increase in aeolian

dust. Additionally, warming events are associated with an increase in river runoff, resulting from a stronger hydrological cycle, which would enhance detrital sediment deposition in general. Such a runoff increase has been suggested as a possible cause for the observed primary production increases observed during the MECO, as it would result in the deliverance of additional nutrients (Boscolo Galazzo et al., 2013; Witkowski et al., 2014).

The second scenario is enhanced organic material preservation caused by oxygen depletion. The Kuma formation is interpreted to be deposited in low-oxygen conditions, explaining the relatively high TOC concentrations throughout (Gavrilov et al., 2000; Benyamovski et al., 2003). Even lower oxygen concentrations during the MECO could result in increased organic matter preservation (Canfield, 1994).

A combination of these two scenarios is plausible, as enhanced primary production is a potential cause of oxygen depletion (Schlanger & Jenkyns, 1976). Further explanations include ocean stratification caused by ocean warming, decreasing oxygen solubility in warmer water and/or poor basin ventilation (Matear & Hirst, 2003), the latter being a possibility as the basin was partially enclosed during the Oligocene, meaning it may have been sensitive to decreased ventilation previously (Van der Boon, 2007).

These scenarios of increase carbon burial are supported by the positive $\delta^{13}C_{carb}$ excursion (Kump & Arthur, 1997). A $\delta^{13}C_{org}$ increase is also expected with increasing productivity, but this is not observed until the negative excursion of approximately 0.5‰ after the peak of the MECO. However, as fractionation increases by about 1‰ during the MECO, a positive organic carbon excursion excursion caused by enhanced production may be masked by higher CO₂ levels leading to more negative $\delta^{13}C$ values, as is discussed in Discussion, section 4.5. Another explanation for the positive excursion of 0.5‰ is a change of organic matter composition, either due to a shift in marine species or due to enhanced terrestrial input, as will be discussed in Discussion section 4.3.

If carbonate deposition remained constant, both organic material and detrital material deposition must have increased almost threefold in order to explain the observed TOC increase and the fact that no change in carbon percentage relative to detrital material is observed. Deposition of both organic and detrital material increasing in such quantities without any observable change in their ratio is highly coincidental, making it less probable that organic matter deposition fully accounts for the observed composition change.

Vanadium and molybdenum concentrations increase simultaneously in the Kuma formation at the Belaya River Section, with a peak near the start of the MECO (Van der Boon, 2017), indicating euxinic conditions throughout the formation and possibly enhanced oxygen depletion around the MECO (Tribovillard et al., 2006). However, the peaks in Va and Mo coincide with the lower part of the high-TOC deposits, not the complete succession, suggesting enhanced euxinic conditions do not account for the high TOC concentrations entirely. Measuring redox-sensitive elements such as manganese and copper could provide more information on whether the peri-Tethys became more oxygen depleted during the MECO (Calvert & Pedersen, 1993). Furthermore, if a high-resolution age model becomes available, sedimentation rates during the MECO can be determined to see whether accumulation rates increased during the MECO, which is expected if the two aforementioned scenarios are correct, as carbonate content would be diluted by enhanced sediment deposition.

4.2.2 Enhanced carbonate deposition scenarios

Reduced carbonate deposition may also the result of a decrease in carbonate production. Possibly, changing environmental conditions, such as warming or the acidification associated with rising CO₂ levels (Zeebe, 2012), negatively impacted calcifying organisms during the MECO. For example, planktic foraminifera appear to have experienced bleaching during the MECO, resulting in dwarfing and a decrease in relative abundance of symbiotic foraminifera , both in the Southern Ocean and in the North Atlantic (Edgar et al., 2013). If specific groups of calcifying organisms indeed declined, this may be observable in assemblages under the microscope.

Enhanced carbonate dissolution after deposition, caused by ocean acidification, could be the cause as well. Ocean acidification caused by rising CO_2 levels during the MECO has been inferred. Around the MECO, carbonate accumulation rates sharply decreased at depths greater than 3000

meters in the Atlantic and Indian Ocean, suggesting deep-ocean acidification and CCD shoaling, while no such decrease was observed at sites located at depths of 2000 m, indicating the CCD was located between 2000 and 3000 m (Bohaty et al., 2009). This suggests that the CCD reaching the Peri-Tethys Ocean, the continental shelf, is an unlikely scenario.

If the observed changes in TOC and carbonate content are the result of a decrease in carbonate deposition, either by reduced production or by enhanced dissolution, this would challenge the hypothesis by Sluijs et al. (2013), which states that carbonate deposition shifted from the deep ocean towards the shelf during the MECO. Even if a decrease in carbonate deposition does not explain the observed sedimentary changes, no evidence for enhanced carbonate deposition was found, meaning the hypothesis is not confirmed.

4.3 Terrestrial input

The BIT index indicates negligible terrestrial input. Care must be taken with this index, however, as the source of brGDGTs, believed to be bacteria, remains elusive (e.g. Sinninghe Damsté et al., 2011; Sun et al., 2016) and brGDGTs may be produced in aquatic environments besides soils (Sinninghe Damsté, 2016; Xiao et al., 2016). However, these uncertainties with regards to the provenance of brGDGTs are mainly an issue when dealing with higher BIT values, not when little to no brGDGTs are found. Nonetheless, soil input may not scale linearly with total terrestrial input (Weijers et al., 2009). Therefore, it is possible that the BIT index is an underestimation of terrestrial input, for example if aeolian dust is a major contributor, but the extremely low brGDGT concentrations deem it unlikely that terrestrial input constitutes a major factor to our CO_2 reconstruction.

This is consistent with the C:N ratios of approximately 14-23, which are plausible values for marine organic matter found in old sediments. Marine algal material typically has C:N ratios between 4 and 10, whereas land plant material has C:N ratios of \geq 20. However, the C:N ratio increases as the material settles through the water column, with marine organic material being altered from 6 to 16 near the eastern coast of South America and even reaching 40 in the Northern Caspian Sea (Hobson & Menzel, 1969; Hyne, 1978). After burial, C:N is altered further, with the average C:N increasing from 10 near the sediment surface to 20 in Eocene strata in three drill holes taken on the upper Florida-Hatteras Slope (Hülsemann, 1968). It is impossible to accurately calculate absolute terrestrial input from C:N ratios in this case, because terrestrial and marine end members are unknown, but numbers between 14 and 23 are consistent with the low terrestrial input suggested by the BIT index.

Since the relative C:N signal is mainly retained in sediments (Meyers, 1994), no considerable shifts in terrestrial input appear to have occurred. A slight increase between 1000 and 1500 cm is observable, but since the start of this shift occurs before the MECO, and since C:N remains stable after the shift, it is unlikely that the observed carbon isotope fractionation increase is a result of terrestrial-plant input. This is supported by the fact that C:N and $\delta^{13}C_{org}$ do not correlate (Figure 7), implying that $\delta^{13}C_{org}$ changes are probably not caused by terrestrial material input. A pilot study on the >15 um fraction of palynological residues of the samples by M. Cramwinckel (pers. comm. 2018) supports this as well: little terrestrial input and no large input changes throughout the section were inferred. Care must be taken with palynology as an indicator, as both species-specific pollen production and transport processes cause potential deviations between palynological results and the actual fraction of terrestrial organic material (Sluijs & Dickens, 2012). However, considering that BIT index, C:N and palynology are based on different sources with different taphonomies, agreement between these three proxies indicates that they are a robust reflection of the fraction of terrestrial organic material present. This suggestion of limited to negligible impact of terrestrial organic carbon on $\delta^{13}C_{org}$ implies that bulk organic material is likely applicable for CO_2 reconstructions, adding reliability to the CO₂ reconstruction. To further exclude the impact of terrestrial organic matter on the final CO₂ reconstruction and make the reconstruction more robust, δ^{13} C of phytane and pristane could be measured for several samples to see if they are in agreement with bulk organic measurements.



Figure 7: $\delta^{13}C_{org}$ plotted against C:N ratio. The red line denotes a linear fit. R², an indication of how close this fit is (where 0 is no fit and 1 is a perfect fit), is 0.038. No correlation is distinguishable.

4.4 Temperature

The observed lack of warming during the MECO, and even the possibility of cooling, is surprising, as the MECO is considered a global warming event (e.g. Bohaty & Zachos, 2003; Bijl et al., 2010). The δ^{18} O data provided in this thesis indicate warming as well, even if no quantitative indication can be extracted from it. There are three explanations for this: either TEX₈₆ does not properly reflect sea surface temperatures, the Peri-Tethys did not warm during the MECO and even may have cooled, or the oxygen isotope excursion does not indicate the MECO after all.

4.4.1 Scenario 1: TEX₈₆ does not reflect temperature

GDGT-2/Crenachaeol reaches 0.11-0.15, approaching the 0.18 matching GDGTs produced in the modern SMTZ within the sediment, meaning it cannot be excluded that Euryarchaeota or other organisms contributed to the GDGT pool, which could cause a temperature overestimation (Weijers et al., 2011). However, as Weijers et al. (2011) explained, this signal is not retained in deeper sediments. In addition, since the ratio does not significantly vary throughout the section, it is expected that this potential effect is constant, deeming it unlikely that a MECO temperature increase would be erased.

The temperatures derived are around 32 °C, which is in agreement with other Eocene temperature records (Evans et al., 2018; Cramwinckel et al., in review). Interestingly, a cooling trend appears to be present. This could correspond to the Eocene cooling trend of the middle to late Eocene, an additional indication that TEX₈₆ contains a temperature signal (Zachos et al., 1993; Cramwinckel et al., unpublished). TEX₈₆ appears to be a primary signal which, unless unknown processes or GDGT-producing organisms interfered, represents temperature and was therefore applied in the CO₂ reconstruction.

4.4.2 Scenario 2: TEX₈₆ correctly reflects temperature

A lack of warming is inconsistent with a TEX₈₆ temperature reconstruction in the southwest Pacific Sea by Bijl et al. (2010) and could only be explained by local effects, such as a relatively colder ocean current entering the basin during the MECO. This would imply a decoupling of δ^{18} O and SST, as the δ^{18} O excursion is interpreted to signal higher temperatures. This could be explained if a significant

part of carbonate does not originate from the sea surface but from depths where temperatures did rise, or by δ^{18} O bearing no temperature signal but a diagenetic signal, as is discussed in section 4.4.3.

To perform additional checks on the temperature results, other temperature proxies could be applied which are independent of carbonates, as these appear to be diagenetically altered significantly. Unfortunately, due to a lack of alkenones in the Belaya record, the temperature proxy $UK_{37}^{k'}$ is not applicable (Prahl & Wakeham, 1987). Possibly, dinoflagellate palynology can indicate whether temperature conditions as well as other environmental conditions changed during the MECO.

4.4.3 Scenario 3: δ^{18} O does not reflect the MECO

In this scenario, discussed in Discussion, section 4.1, the cooling trend observed could be the climate recovering from peak-MECO conditions and the outlier from this trend at 900 cm corresponds to the temperature increase associated with the MECO. Performing more TEX₈₆ measurements would reveal if a temperature peak indeed is present underneath the oxygen isotope excursion or confirm whether an overall cooling trend is found.

4.5 CO₂ reconstruction

Considering that the organic material in the Belaya sediments appears to be primarily marine and a distinct and consistent ϵ_p increase of approximately 1‰ coincides with the MECO, a CO₂ reconstruction was performed, applying the reconstructed temperatures. ϵ_f and b-values could not be directly estimated, meaning a conservative range of of 25-28‰ and 100-200 were applied, respectively (based on literature, see Materials & Methods, section 2.5).

The CO₂ reconstruction (Figure 8) indicates CO₂ levels of 500-1750 ppmv before, 550-2100 ppmv during and 400-1600 directly after the MECO. When assuming a constant *b*-value and ε_f , the reconstruction indicates a minimum CO₂-concentration increase of 50 ppmv and a maximum of 350 ppmv during the MECO. Assuming an ε_f towards 25‰ and *b*-values towards 200 culminates in significantly higher relative CO₂ level rises than assuming a higher ε_f and lower *b*-values.

Nevertheless, due to large uncertainties in *b*-value and ε_f , it is impossible to draw insightful quantitative conclusions about an absolute CO₂ increase. Theoretically, relative CO₂ level changes cannot be determined when considering the full range of uncertainties, as minimum estimations never approach maximum estimations. Bijl et al. (2010) and Naafs et al. (2016) show similar uncertainties in their CO₂ reconstructions, but manage to show a significant CO₂ increase due to a more pronounced ε_p difference between pre-MECO and MECO times. In practice, however, the results presented in this thesis do qualitatively suggest a CO₂ increase during the MECO, as is explained below.

4.5.1 Effect of ϵ_f on CO₂ reconstruction

 $\varepsilon_{\rm f}$, the theoretical maximum fractionation by RuBisCO, is a major uncertainty in the reconstruction, significantly affecting both absolute CO₂ levels and relative CO₂ changes (Figure 8). In modern day oceans, $\varepsilon_{\rm f}$ is about 25‰ for a variety of microorganisms (Popp et al., 1998; Pagani et al., 2002). This is also the $\varepsilon_{\rm f}$ -value applied in other CO₂ reconstructions (e.g. Bijl et al., 2010; Naafs et al., 2016) and one of the scenarios shown in Figure 8. However, as recommended by Pagani (2002), the conservative range of 25-28‰ was used because $\varepsilon_{\rm f}$ cannot be constrained for past algal communities. To fully account for the $\varepsilon_{\rm p}$ increase measured, a rise of about 1‰ during the MECO is needed. However, although absolute $\varepsilon_{\rm f}$ could not be constrained, it is reasonable to assume that $\varepsilon_{\rm f}$ remained constant on this timescale considering that RuBisCO I (which operates in cyanobacteria and choloplasts) in its current complexity is at least several hundred Ma old and does not appear to have undergone significant evolutionary changes since (Erb & Zarzycki, 2018).

4.5.2 Effect of b-value on CO₂ reconstruction

The *b*-value is another major uncertainty because it was not estimated in this thesis, meaning a broad range of 100-200 was applied. As is the case with ε_f , there is no certainty about absolute values, but a decrease of several 10s during the MECO is needed to account for the ε_p shift. Instead,

if primary production indeed increased during the MECO, as is suggested by data from other Tethys sites and possibly by the rise in TOC established in the Belaya River Section, an increase in *b*-value is expected during the MECO instead of a decrease (Bidigare, 1999). This would result in a more pronounced CO_2 -level rise during the MECO, as can be seen in Figure 8. To acquire more certainty on potential *b*-value changes, productivity can be reconstructed using marine palynology, or $\delta^{15}N$ can be measured to estimate *b*.

4.5.3 Effect of temperature on CO₂ reconstruction

Since the reconstructed temperatures indicate an unexpected lack of warming, the effects of different temperatures on the CO_2 reconstruction must be considered. If the reconstructed temperatures turn out to be incorrect and an increase in temperature did actually occur, the suggested CO_2 -level rise would be enhanced during the MECO (see Figure 8). The fact that an increase in CO_2 concentration can still be inferred without a temperature increase only adds confidence that an actual CO_2 rise is inferred.



Figure 8: CO₂ reconstruction (in purple) and three CO₂ scenarios under alternative assumptions (in orange). Graph 1 shows the reconstruction under the conditions set in Materials & Methods (section 2.5), with minimum and maximum CO₂ levels showing the extreme ends when incorporating analytical and methodological errors of $\delta^{13}C_{carb}$, $\delta^{13}C_{org}$ and SST, *b*-values of 100-200, and ε_f of 25-28‰. The line in the centre uses the average of all factors, incorporating a *b*-value of 150 and a ε_f of 26.5. Graph 2, 3 and 4 shown the same reconstructions, altering one parameter to show the effects of different assumptions on the minimum, mean and maximum CO₂ reconstructions. Graph 2 assumes a constant ε_f of 25‰. Graph 3 assumes constant temperatures of 30 °C with an abrupt increase to 34 °C during the MECO. Graph 4 assumes a *b*-value increase of 30 on top of the originally assumed *b*-values (100, 150 and 200) during the MECO. Data is plotted in the depth domain, starting at 800 meters.

4.5.4 Implications of CO₂ reconstruction

In conclusion, the data suggests CO_2 levels were elevated during the MECO. If the factors discussed above did not remain constant, their respective changes would most likely enhance the reconstructed CO_2 -level rise instead of subduing it. The reconstruction is consistent with the CO_2 increase already inferred by Bijl et al. (2010).

All reconstructions suggest a rise in the order of hundreds of ppmv. This is inconsistent with Bijl et al. (2010), who found an increase in the order of thousands of ppmv, their best estimate being 2000-3000 ppmv. CO_2 -levels of this magnitude, with levels of at least 4000 ppmv, does not match with Eocene CO_2 -levels inferred by Pagani et al. (2005) (700-2000 ppmv) and Anagnostou et al. (2016) (500-1700 ppmv), or those compiled by Gehler et al., (2016) (100-1200 ppmv; one outlier reaching 3000 ppmv). The magnitude of the CO_2 concentrations found in this thesis fit the literature more closely.

Nonetheless, the outcome of this thesis confirms that the MECO was associated with increasing CO_2 levels and suggests that CO_2 levels remained elevated throughout the event. This persistence of high CO_2 levels implies that the exceptional duration of the MECO is the result of an extended period of continuous CO_2 emission, an extended period where CO_2 drawdown was withheld, or a combination.

The remaining question is what caused CO_2 levels to increase and remain elevated. As the MECO is not associated with a convincing, global negative $\delta^{13}C$ excursion, it is unlikely that methane hydrates were a major source of greenhouse gases, as is probable in the case of the PETM (Sluijs et al., 2007). One possibility is extrusive continental-arc volcanism in present-day Iran, as Ar-Ar dating of volcanic rocks indicates volcanism to have taken place there at approximately 40 Ma (Van der Boon 2017). This hypothesis can be further tested by measuring mercury concentrations in the Belaya samples, as higher mercury concentrations may indicate enhanced volcanic activity (Sial et al., 2013). Another suggestion is enhanced metamorphic alteration of carbonates due to subduction of carbonate-rich oceanic plates in the Himalayan orogen (Bohaty & Zachos, 2003). As Bohaty & Zachos (2003) pointed out, better age constraints on this metamorphic activity would help to test this hypothesis.

5. Conclusions

 CO_2 changes during the MECO were studied by performing a CO_2 reconstruction based on carbon isotope fractionation (ϵ_p) of marine primary producers. $\delta^{18}O$ values were measured to determine the stratigraphic position of the MECO, which is represented by a negative $\delta^{18}O$ excursion globally. In order to determine ϵ_p and CO_2 concentrations, $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ were measured and sea surface temperatures were reconstructed using TEX₈₆. The *b*-value and ϵ_f , influencers of ϵ_p , were estimated based on literature. To examine the impact of terrestrial organic matter input, C:N ratios and the BIT index were applied. Further insights on the environmental impact of the MECO were acquired by estimating carbonate content during decalcification and TOC from mass spectrometry measurements.

A distinct negative δ^{18} O excursion of ~2‰ in the Kuma formation is interpreted to represent the MECO. As δ^{18} O is expected to be diagenetically altered significantly, due to the negative values of -6 to -4‰, it is only applicable as a chemostratigraphic marker, not as temperature proxy. Coinciding with the oxygen isotope excursion, $\delta^{13}C_{carb}$ shows a positive excursion. This may be the same excursion encountered in other MECO-containing sections, including several from the Western Tethys, and it may be caused by enhanced carbon burial. Negative carbon isotope excursions encountered in other MECO records are not present, suggesting the association of the MECO with one or more negative carbon isotope excursions may not be a global phenomenon, although it may also be a consequence of resolution issues.

Coinciding with the oxygen isotope excursion, TOC levels increase from approximately 3% to 5-6% and carbonate concentrations decrease from around 60% to 30-40%. One explanation for this is enhanced organic matter deposition due to higher productivity, decreased oxygen concentrations, or a combination. The fact that organic carbon content does not increase relative to detritic material shows that for this to be true, detritic deposition must have increased with the same factor as organic matter deposition, which is dubious. The second explanation is decreased carbonate deposition as a result of lower carbonate production or enhanced dissolution. If this is correct, it opposes the hypothesis that carbonate deposition shifted from the deep ocean to the shelf in this

particular location of the Tethys. Studying the composition of calcifying micro-organisms with a microscope may provide additional clues to see whether this is possible.

All terrestrial-input indicators suggest a stable, low input of terrestrial organic material. This suggests that $\delta^{13}C_{org}$ primarily reflects a marine signal, implying that bulk $\delta^{13}C_{org}$ is applicable to perform CO₂ reconstructions. This is supported by the lack of correlation between $\delta^{13}C_{org}$ and C:N.

While a temperature increase during the MECO is expected, TEX₈₆ indicates a cooling trend throughout the MECO. GDGT compositions show no convincing problems with processes that impact TEX₈₆ independently of temperature, the BIT index indicates negligible input of terrestrial GDGTs, successful duplications show analytical robustness and the temperatures of ~32 °C are consistent with other Eocene records. Therefore, the temperatures were applied in the CO₂ reconstruction. Possibly, a local change in ocean currents accounts for the observed lack of warming or even cooling. Other options are unforeseen geochemical or biological factors impacting TEX₈₆ independent of temperature and the possibility that the δ^{18} O excursion does not represent the MECO due to diagenetic alterations. The latter seems unlikely, however, because ε_p also suggests that this interval represents the MECO. Until an age model is constructed, however, no absolute certainty can be given regarding this matter.

 ϵ_p shows a robust increase of ~1‰ during the MECO. This is reflected in the CO₂ reconstruction, which infers CO₂-levels of 500-1750 ppmv before, 550-2100 ppmv during and 400-1600 after the MECO, which is consistent with the literature, and an increase in the order of hundreds of ppmv. However, due to large uncertainties, mainly in ϵ_f and the *b*-value, few quantitative conclusions can be drawn from this reconstruction. Nonetheless, unless ϵ_f unexpectedly changed in a short period of time or if *b* decreased for unexpected reasons, ϵ_p most likely represents a CO₂ signal. If the temperature reconstruction appears incorrect and warming did take place during the MECO, this would further enhance ϵ_p and thereby reconstructed CO₂ levels during the MECO. If *b*-values did not remain constant, it is expected to increase during the MECO rather than decrease, thereby enhancing the reconstructed CO₂-level increase as well.

This CO_2 -level rise supports the hypothesis that the MECO was caused by rising CO_2 levels, possibly due to volcanism in present-day Iran. It also suggests that CO_2 levels remained high for an extended period, either due to continuous input or reduced CO_2 drawdown compared to other warming events, or a combination.

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Appendices

Appendix 1: Bulk-carbonate oxygen isotope measurements

Corrected for peak height



Cumulative position (cm)	δ18Ο (‰)	stdev (‰)	Cum. pos. (cm)	δ18Ο (‰)	stdev (‰)
513	-3.25	0.127	1025	-3.77	0.127
52	-3.50	0.127	1041	-3.47	0.127
53	-3.34	0.127	1052	-3.50	0.127
54	-3.68	0.127	1063	-3.60	0.127
55	-3.47	0.127	1063	-3.53	0.127
56	-2.95	0.127	1080	-3.71	0.127
573	-3.33	0.127	1087	-3.78	0.127
592	-3.27	0.127	1096	-3.59	0.127
61	-3.05	0.127	1105	-3.58	0.127
624	-3.48	0.127	1125	-4.05	0.127
624	-3.48	0.127	1135	-3.82	0.101
63:	-3.23	0.127	1146	-3.69	0.101
64	-3.61	0.127	1165	-3.89	0.101
65	-3.66	0.127	1180	-3.88	0.101
662	-3.46	0.127	1190	-3.98	0.101
69!	-3.27	0.127	1200	-4.21	0.101
702	-3.09	0.127	1215	-3.95	0.101
718	-3.42	0.127	1228	-4.16	0.101
73	-3.27	0.127	1240	-4.01	0.101
74	-3.22	0.127	1252	-4.15	0.101
76	-3.53	0.127	1273	-4.44	0.101
76	-3.31	0.127	1280	-4.44	0.101
78	-3.16	0.127	1284	-4.24	0.101
81	-3.60	0.127	1295	-5.12	0.101
81	-3.59	0.127	1310	-5.32	0.101
82	-3.47	0.127	1319	-4.16	0.101
83	-3.05	0.127	1331	-5.69	0.101
	-3.70	0.127	1343	-5.19	0.101
85	-3.78	0.127	1354	-5.20	0.101
88	-3.42	0.127	1369	-5.64	0.101
89:	-3.41	0.127	1378	-5.06	0.101
90	-3.61	0.127	1380	-5.63	0.101
90	-3.86	0.127	1393	-4.88	0.101
91	-3.13	0.127	1396	-4.92	0.101
92	-3.52	0.127	1400	-5.18	0.101
93	-4.02	0.127	1405	-5.37	0.101
950	-4.14	0.127	1418	-5.74	0.101
950	-3.55	0.127	1433	-5.75	0.101
95	-4.04	0.127	1443	-5.70	0.101
97	-3.48	0.127	1451	-5.69	0.101
98	-3.73	0.127	1461	-5.60	0.101
99	-3.42	0.127	1470	-5.63	0.101
1004	-4.37	0.127	1477	-5.41	0.101
101	-3.55	0.127	1498	-6.34	0.101

Cumulative position (cm)	δ18Ο (‰)	stdev (‰)
1508	-5.73	0.101
1515	-5.59	0.101
1536	-4.81	0.101
1548	-3.81	0.101
1555	-5.21	0.101
1565	-4.89	0.101
1578	-3.95	0.101
1585	-3.60	0.101
1591	-3.42	0.101
1597	-3.67	0.101
1605	-4.40	0.101
1625	-3.69	0.101
1652	-4.61	0.101
1672	-4.66	0.101
1693	-4.14	0.101
1706	-3.59	0.101
1729	-4.65	0.101
1749	-3.57	0.101
1782	-4.33	0.101
1830	-4.13	0.101
1865	-4.05	0.101
1891	-3.66	0.101
1935	-3.65	0.101
1955	-4.19	0.101
1980	-3.35	0.067
2015	-3.32	0.067
2050	-3.17	0.067
2138	-3.23	0.067
2183	-2.99	0.067
2201	-3.19	0.067
2223	-3.06	0.067
2248	-2.93	0.067
2273	-3.34	0.067
2293	-3.19	0.067
2343	-3.09	0.067
2380	-3.20	0.067
2455	-3.13	0.067
2520	-3.01	0.067
2605	-3.30	0.067
2655	-3.17	0.067

Appendix 2: Bulk-carbonate carbon isotope measurements

Corrected for peak height



Cumulative position (cm)	δ13C (‰)	stdev (‰)	Cum. pos. (cm)	δ13C (‰)	stdev (‰)
513	1.69	0.144	1025	1.41	0.144
521	1.58	0.144	1041	1.61	0.144
530	1.52	0.144	1052	1.64	0.144
540	1.20	0.144	1063	1.47	0.144
550	1.44	0.144	1063	1.40	0.144
563	1.55	0.144	1080	1.29	0.144
572	1.47	0.144	1087	1.05	0.144
592	1.68	0.144	1096	1.14	0.144
610	1.42	0.144	1105	1.06	0.144
624	1.43	0.144	1125	1.30	0.144
624	1.39	0.144	1135	1.62	0.075
631	1.42	0.144	1146	1.63	0.075
640	1.08	0.144	1165	1.26	0.075
650	1.19	0.144	1180	1.22	0.075
662	1.61	0.144	1190	1.20	0.075
695	1.49	0.144	1200	1.30	0.075
702	1.36	0.144	1215	1.53	0.075
718	1.20	0.144	1228	1.28	0.075
738	1.26	0.144	1240	1.35	0.075
748	1.44	0.144	1252	1.37	0.075
760	1.43	0.144	1273	1.43	0.075
768	1.27	0.144	1280	1.30	0.075
780	1.32	0.144	1284	1.35	0.075
810	1.42	0.144	1295	1.25	0.075
815	1.26	0.144	1310	0.92	0.075
828	1.73	0.144	1319	1.24	0.075
837	1.60	0.144	1331	1.31	0.075
847	1.26	0.144	1343	1.65	0.075
857	1.18	0.144	1354	1.66	0.075
881	1.62	0.144	1369	1.75	0.075
891	1.38	0.144	1378	2.06	0.075
903	1.26	0.144	1380	1.90	0.075
908	1.52	0.144	1393	2.05	0.075
915	1.56	0.144	1396	1.98	0.075
925	1.41	0.144	1400	2.09	0.075
935	1.01	0.144	1405	1.86	0.075
950	0.82	0.144	1418	1.65	0.075
950	1.18	0.144	1433	1.78	0.075
957	1.04	0.144	1443	2.37	0.075
970	1.58	0.144	1451	2.34	0.075
985	1.28	0.144	1461	2.46	0.075
997	1.27	0.144	1470	2.54	0.075
1004	1.11	0.144	1477	2.00	0.075
1015	1.10	0.144	1498	1.61	0.075

Cumulative position (cm)	δ13C (‰)	stdev (‰)
1508	1.90	0.075
1515	1.86	0.075
1536	2.19	0.075
1548	1.76	0.075
1555	2.16	0.075
1565	1.68	0.075
1578	1.14	0.075
1585	1.58	0.075
1591	1.55	0.075
1597	1.25	0.075
1605	1.54	0.075
1625	1.81	0.075
1652	1.72	0.075
1672	0.84	0.075
1693	1.42	0.075
1706	1.85	0.075
1729	1.37	0.075
1749	1.62	0.075
1782	1.45	0.075
1830	1.93	0.075
1865	1.79	0.075
1891	1.35	0.075
1935	1.50	0.075
1955	1.04	0.075
1980	1.67	0.083
2015	1.46	0.083
2050	1.53	0.083
2138	1.57	0.083
2183	1.79	0.083
2201	1.95	0.083
2223	1.73	0.083
2248	1.69	0.083
2273	1.58	0.083
2293	1.82	0.083
2343	1.69	0.083
2380	1.95	0.083
2455	2.01	0.083
2520	2.12	0.083
2605	1.87	0.083
2655	1.91	0.083

Appendix 3: Bulk-organic carbon isotope measurements

Corrected for peak height



Cumulative position (cm)	δ13C (org) (‰)	stdev (‰)	Cum. pos. (cm)	δ13C (org) (‰)	stdev (‰)
0	-26.80	0.075	828	-26.72	0.075
32	-26.79	0.075	837	-26.87	0.075
58	-26.45	0.075	847	-26.85	0.075
105	-27.01	0.075	857	-27.21	0.075
114	-26.77	0.075	881	-26.26	0.075
138	-26.76	0.075	891	-27.21	0.075
152	-26.34	0.075	903	-27.23	0.075
196	-26.94	0.075	908	-27.16	0.075
215	-27.00	0.075	915	-26.92	0.075
248	-27.27	0.075	925	-26.95	0.075
292	-26.99	0.075	935	-27.04	0.075
308	-27.13	0.075	950	-27.21	0.075
328	-27.15	0.075	950	-27.06	0.075
343	-27.37	0.075	957	-27.07	0.075
373	-26.57	0.075	970	-26.94	0.075
398	-26.15	0.075	985	-26.68	0.075
428	-26.84	0.075	997	-26.78	0.075
473	-26.84	0.075	1004	-26.83	0.075
513	-26.91	0.075	1015	-27.04	0.115
521	-27.07	0.075	1025	-26.87	0.075
530	-27.22	0.075	1041	-27.01	0.075
540	-27.25	0.075	1052	-26.81	0.075
550	-27.13	0.075	1063	-26.52	0.075
563	-27.06	0.075	1063	-27.05	0.115
572	-27.13	0.075	1080	-26.99	0.115
592	-27.29	0.075	1087	-26.44	0.115
610	-27.24	0.075	1096	-26.96	0.115
624	-27.42	0.115	1105	-26.83	0.115
624	-27.39	0.075	1114	-27.14	0.115
631	-26.56	0.115	1125	-26.96	0.115
640	-26.91	0.075	1135	-26.99	0.115
650	-27.24	0.075	1146	-26.84	0.115
662	-27.16	0.075	1165	-27.22	0.115
695	-27.06	0.075	1180	-27.31	0.115
702	-27.12	0.075	1190	-26.99	0.115
718	-27.34	0.115	1200	-26.79	0.115
738	-26.88	0.075	1215	-26.96	0.115
748	-27.08	0.075	1228	-27.00	0.115
760	-27.27	0.075	1240	-27.06	0.115
768	-27.36	0.115	1252	-27.01	0.115
780	-26.99	0.075	1268	-27.05	0.115
795	-26.97	0.075	1273	-27.06	0.115
810	-26.98	0.075	1280	-27.05	0.115
815	-27.28	0.075	1284	-27.23	0.115

Cumulative position (cm)	δ13C (org) (‰)	stdev (‰)	Cum. pos. (cm)	δ13C (org) (‰)	stdev (‰)
1295	-27.15	0.115	1955	-26.11	0.161
1310	-27.03	0.115	1980	-26.96	0.115
1319	-27.04	0.115	2015	-26.62	0.115
1331	-27.15	0.115	2050	-26.64	0.115
1343	-27.37	0.115	2080	-26.75	0.115
1354	-27.27	0.161	2109	-27.04	0.115
1369	-27.29	0.161	2138	-27.20	0.115
1378	-27.26	0.161	2166	-27.08	0.115
1380	-27.43	0.115	2183	-26.92	0.115
1393	-27.15	0.115	2201	-27.12	0.115
1396	-27.11	0.161	2223	-27.02	0.115
1400	-26.91	0.161	2248	-26.90	0.115
1405	-27.21	0.115	2273	-27.10	0.115
1418	-27.44	0.161	2293	-26.93	0.115
1433	-27.35	0.161	2343	-26.54	0.115
1443	-27.04	0.161	2380	-26.82	0.115
1451	-27.02	0.161	2455	-26.66	0.115
1461	-26.95	0.161	2520	-26.58	0.115
1470	-27.07	0.161	2605	-27.35	0.115
1477	-26.84	0.161	2655	-27.18	0.115
1498	-27.39	0.115	2725	-26.95	0.115
1508	-27.00	0.115	2775	-27.49	0.115
1515	-26.91	0.161	2815	-27.38	0.115
1536	-26.05	0.161	2870	-27.10	0.115
1548	-26.55	0.161			
1555	-26.64	0.161			
1565	-26.27	0.161			
1578	-26.39	0.161			
1585	-26.48	0.161			
1591	-26.52	0.161			
1597	-26.55	0.161			
1605	-26.63	0.161			
1625	-26.48	0.161			
1652	-26.48	0.161			
1672	-26.77	0.161			
1693	-26.29	0.115			
1706	-26.25	0.115			
1729	-26.30	0.161	l		
1749	-26.97	0.161	l		
1782	-26.55	0.161	l		
1830	-26.85	0.161	l		
1865	-26.56	0.161			
1891	-27.16	0.161			
1935	-26.95	0.161]		

Appendix 4: Sedimentary composition

Cumulative position (m)	Carbonate (%)	%C (decal)	error %C (decal)	%N (decal)	error %N	C:N	TOC (%)
0	73.19	13.72	0.95	0.69	940.73	20.00	3.68
32	74.59	13.01	0.90	0.61	789.01	21.46	3.31
58	83.20	13.81	0.95	0.75	1040.70	18.31	2.32
105	69.09	11.23	0.78	0.61	688.12	18.34	3.47
114	70.09	10.91	0.75	0.67	735.14	16.18	3.26
138	66.09	9.47	0.65	0.49	466.33	19.25	3.21
152	75.17	10.44	0.72	0.55	571.00	19.09	2.59
196	68.93	8.91	0.61	0.49	434.86	18.26	2.77
215	67.92	9.17	0.63	0.52	474.45	17.73	2.94
248	70.76	8.17	0.56	0.45	369.33	18.09	2.39
292	60.30	7.23	0.50	0.46	329.05	15.86	2.87
308	61.31	4.69	0.32	0.28	132.26	16.64	1.82
328	60.30	7.54	0.52	0.54	403.24	14.08	2.99
343	65.21	7.44	0.51	0.41	301.51	18.38	2.59
373	56.58	12.97	0.90	0.71	926.60	18.17	5.63
398	59.10	7.56	0.52	0.40	303.64	18.80	3.09
428	55.00	7.53	0.52	0.41	306.33	18.50	3.39
473	54.34	7.68	0.53	0.51	392.47	15.03	3.51
513	58.24	7.83	0.54	0.37	288.68	21.22	3.27
521	57.51	8.04	0.55	0.51	410.91	15.73	3.42
530	59.81	7.89	0.54	0.47	371.53	16.77	3.17
540	57.09	7.64	0.53	0.45	342.58	17.02	3.28
550	57.54	7.41	0.51	0.44	323.68	16.96	3.15
563	59.33	7.36	0.51	0.37	273.64	19.78	2.99
572	61.21	7.17	0.49	0.44	317.29	16.21	2.78
592	58.02	8.08	0.56	0.45	363.20	17.99	3.39
610	57.40	6.82	0.47	0.42	289.30	16.09	2.91
624	56.09	7.56	0.59	0.34	259.83	22.01	3.32
624	55.22	5.37	0.37	0.27	145.59	19.84	2.41
631	58.53	7.63	0.60	0.37	280.70	20.76	3.17
640	67.88	8.23	0.57	0.43	356.58	19.01	2.64
650	55.57	6.93	0.48	0.48	333.47	14.41	3.08
662	52.82	7.29	0.50	0.42	304.20	17.49	3.44
695	57.22	6.06	0.42	0.42	256.84	14.30	2.59
702	56.18	6.92	0.48	0.51	354.52	13.52	3.03
718	57.02	6.66	0.52	0.37	245.15	18.08	2.86
738	59.95	7.88	0.54	0.47	370.83	16.73	3.15
748	55.39	6.60	0.46	0.43	287.10	15.18	2.95
760	55.66	7.07	0.49	0.39	276.23	18.08	3.13

Carbonate content, %C (decalcified), %N (decalcified), C:N and TOC

Cumulative position (m)	Carbonate (%)	%C (decal)	error %C (decal)	%N (decal)	error %N	C:N	TOC (%)
768	59.58	6.14	0.48	0.39	237.18	15.89	2.48
780	61.07	6.69	0.46	0.45	303.35	14.75	2.60
795	63.30	6.48	0.45	0.41	262.68	15.96	2.38
810	61.20	7.52	0.52	0.48	363.76	15.53	2.92
815	57.65	7.16	0.49	0.52	373.14	13.76	3.03
828	59.71	7.03	0.49	0.44	311.21	15.88	2.83
837	61.19	6.67	0.46	0.39	257.12	17.29	2.59
847	54.47	6.87	0.47	0.44	300.77	15.71	3.13
857	57.91	7.29	0.50	0.51	372.81	14.27	3.07
881	57.57	7.79	0.54	0.49	384.64	15.76	3.30
891	57.36	6.87	0.47	0.41	283.70	16.64	2.93
903	54.44	7.47	0.52	0.46	340.32	16.39	3.40
908	62.79	7.88	0.54	0.55	433.07	14.33	2.93
915	58.78	7.11	0.49	0.43	307.91	16.42	2.93
925	61.98	7.36	0.51	0.49	362.66	14.94	2.80
935	56.71	6.75	0.47	0.43	292.21	15.58	2.92
950	62.63	7.70	0.53	0.51	392.59	15.11	2.88
950	62.47	8.11	0.56	0.54	436.28	15.06	3.04
957	54.90	6.83	0.47	0.49	332.24	14.05	3.08
970	58.85	6.21	0.43	0.42	260.08	14.82	2.56
985	59.58	7.54	0.52	0.47	358.09	15.89	3.05
997	59.75	6.92	0.48	0.43	300.24	15.96	2.79
1004	58.75	6.29	0.43	0.45	282.95	13.96	2.59
1015	55.36	5.88	0.46	0.34	197.40	17.50	3.30
1025	59.61	7.39	0.51	0.42	313.80	17.38	3.05
1041	59.99	7.55	0.52	0.49	367.18	15.54	3.02
1052	66.69	7.61	0.52	0.51	390.96	14.79	2.53
1063	62.32	7.37	0.51	0.50	366.34	14.82	2.78
1063	64.36	6.20	0.49	0.32	199.69	19.28	2.21
1080	60.28	7.16	0.56	0.39	281.19	18.21	2.84
1087	61.75	7.84	0.62	0.44	348.17	17.67	3.00
1096	61.79	7.87	0.62	0.45	352.98	17.52	3.00
1105	59.98	6.60	0.52	0.39	259.07	16.79	2.64
1114	62.89	7.27	0.34	0.50	361.76	14.62	2.70
1125	64.50	6.65	0.52	0.35	234.15	18.86	2.36
1135	62.22	6.42	0.50	0.45	289.80	14.24	2.43
1146	59.57	6.93	0.54	0.39	266.65	17.99	2.80
1165	57.20	6.97	0.55	0.45	317.26	15.33	2.98
1180	60.78	7.61	0.60	0.40	306.55	18.90	2.99
1190	61.49	7.71	0.61	0.44	339.36	17.53	2.97
1200	59.64	8.26	0.65	0.47	391.42	17.45	3.34
1215	59.50	8.05	0.63	0.43	348.30	18.63	3.26
1228	62.80	7.53	0.59	0.46	347.96	16.28	2.80
1240	59.15	7.46	0.59	0.39	291.05	19.13	3.05

Cumulative position (m)	Carbonate (%)	%C (decal)	error %C (decal)	%N (decal)	error %N	C:N	TOC (%)
1252	54.33	8.20	0.64	0.42	346.39	19.39	3.74
1268	54.43	7.61	0.60	0.45	341.74	16.93	3.47
1273	56.12	8.40	0.66	0.48	399.67	17.67	3.69
1280	57.14	7.72	0.61	0.44	340.67	17.50	3.31
1284	59.10	7.67	0.60	0.40	307.04	19.14	3.14
1295	57.85	8.06	0.63	0.42	341.57	19.01	3.40
1310	63.55	8.18	0.64	0.48	389.81	17.16	2.98
1319	66.45	7.99	0.63	0.45	356.37	17.92	2.68
1331	46.72	8.60	0.68	0.47	400.90	18.45	4.58
1343	34.58	8.57	0.67	0.40	342.09	21.49	5.61
1354	46.27	10.06	1.21	0.48	484.93	20.88	5.41
1369	37.79	8.96	1.08	0.50	445.23	18.03	5.57
1378	43.27	9.63	1.16	0.40	381.91	24.29	5.46
1380	40.69	8.58	0.67	0.38	322.44	22.84	5.09
1393	46.87	8.52	0.67	0.46	389.28	18.64	4.53
1396	44.77	8.85	1.07	0.47	412.57	18.98	4.89
1400	44.16	9.35	1.13	0.42	391.31	22.35	5.22
1405	37.61	7.90	0.62	0.37	288.64	21.61	4.93
1418	34.80	8.93	1.08	0.58	513.88	15.51	5.82
1433	38.45	10.41	1.25	0.49	514.63	21.06	6.41
1443	35.18	9.21	1.11	0.46	423.48	20.05	5.97
1451	34.23	9.36	1.13	0.39	363.79	24.10	6.16
1461	33.29	8.11	0.98	0.38	304.35	21.59	5.41
1470	33.01	9.02	1.09	0.46	417.30	19.49	6.04
1477	33.66	9.24	1.11	0.44	405.34	21.07	6.13
1498	34.67	8.90	0.70	0.44	392.85	20.17	5.82
1508	41.09	9.46	0.74	0.47	443.53	20.17	5.57
1515	40.08	10.52	1.27	0.50	531.10	20.85	6.31
1536	49.39	9.97	1.20	0.42	414.68	23.97	5.05
1548	54.01	7.14	0.86	0.41	295.04	17.28	3.28
1555	47.98	9.29	1.12	0.49	458.75	18.82	4.83
1565	48.54	8.84	1.07	0.46	407.84	19.17	4.55
1578	64.99	8.08	0.97	0.40	320.87	20.36	2.83
1585	63.39	8.21	0.99	0.37	302.06	22.33	3.01
1591	63.56	7.87	0.95	0.37	293.67	21.10	2.87
1597	65.96	8.01	0.97	0.38	303.80	21.14	2.73
1605	59.85	9.55	1.15	0.49	466.42	19.57	3.84
1625	58.67	9.18	1.11	0.44	405.68	20.76	3.79
1652	57.32	10.41	1.25	0.50	522.58	20.73	4.44
1672	63.53	8.53	1.03	0.47	401.48	18.12	3.11
1693	63.66	8.61	0.68	0.40	342.99	21.60	3.13
1706	66.83	9.32	0.73	0.48	451.74	19.22	3.09
1729	60.21	9.84	1.19	0.43	423.62	22.86	3.92
1749	64.27	8.78	1.06	0.46	402.42	19.14	3.14

Cumulative position (m)	Carbonate (%)	%C (decal)	error %C (decal)	%N (decal)	error %N	C:N	TOC (%)
1782	62.86	9.65	1.16	0.45	434.45	21.44	3.58
1830	57.75	10.47	1.26	0.56	591.56	18.54	4.42
1865	64.38	11.26	1.36	0.49	555.84	22.81	4.01
1891	66.35	9.48	1.14	0.50	478.06	18.80	3.19
1935	67.11	9.96	1.20	0.49	485.32	20.44	3.28
1955	71.09	11.78	1.42	0.49	573.56	24.20	3.41
1980	68.92	9.86	0.77	0.47	464.17	20.95	3.07
2015	71.99	11.03	0.87	0.45	496.04	24.54	3.09
2050	69.46	12.03	0.94	0.46	547.97	26.40	3.67
2080	74.65	10.03	0.79	0.43	428.37	23.50	2.54
2109	60.10	9.23	0.73	0.42	390.52	21.83	3.68
2138	59.70	9.04	0.71	0.40	358.69	22.77	3.64
2166	62.15	9.75	0.77	0.43	422.15	22.53	3.69
2183	63.40	9.41	0.74	0.41	388.81	22.78	3.44
2201	63.31	10.17	0.80	0.48	492.38	20.99	3.73
2223	65.76	9.21	0.72	0.42	389.70	21.77	3.15
2248	76.44	13.35	1.05	0.56	748.44	23.81	3.14
2273	69.50	9.92	0.78	0.38	377.86	26.03	3.02
2293	69.53	11.07	0.87	0.53	581.39	21.08	3.37
2343	67.41	9.78	0.77	0.44	429.17	22.27	3.19
2380	61.13	9.37	0.74	0.42	395.41	22.20	3.64
2455	63.45	9.68	0.76	0.42	409.76	22.86	3.54
2520	57.54	10.36	0.81	0.49	506.14	21.21	4.40
2605	64.52	8.30	0.65	0.38	314.53	21.92	2.95
2655	62.86	9.13	0.72	0.42	385.17	21.63	3.39
2725	59.62	9.43	0.74	0.41	382.55	23.24	3.81
2775	71.65	9.96	0.78	0.42	418.78	23.67	2.82
2815	65.41	9.72	0.76	0.46	445.74	21.20	3.36
2870	71.91	10.92	0.86	0.47	512.22	23.30	3.07

	Isoprenoid GDGTs (Area)									
	GDGT-0 (II) GDGT-1 (III) GDGT-2 (IV) GDGT-3 (V) GDGT-4 (= Crenarcheol)									
Stratigraphic position (cm)	1302	1300	1298	1296	1292 (I)	1292' (VI)				
903	55885.9	21124	42777	9068	392594	45143				
997	41997.7	17275.3	41661.6	8597.79	307729	45406.8				
1096	52145.7	21121.2	49225.9	10387.3	389107	58539.6				
1215	59891.7	23671.2	50539.9	10951.9	386542	53540.5				
1280	60109.5	21169.6	42066.9	10448.8	341970	46245.5				
1319	73208.8	28440.4	66133.4	14629.1	531258	78764.1				
1343	61500.8	24118.3	46119.9	12142.6	394688	55052.6				
1380	48101.9	17142.5	33583.5	9105.2	259210	31009.6				
1405	81966.3	30579.3	57808.2	14322.4	461369	64482.1				
1451	95070.1	34537	58593.4	13893.5	458418	51496.4				
1470	74494.6	25757.8	44005.4	10607.1	359761	43278.9				
1498	138193	52762.5	111113	26919.3	859020	109402				
1548	237072	22818.9	41480.3	9398.36	294212	35144.5				
1585	70037.5	24813.5	45581.6	9642.22	318762	37762.1				
1625	57320	19860	36482.4	8392.27	266197	31023.9				
1706	657897	30572.2	63509	12815.7	428283	52841.8				
1830	42574.6	15630.3	32213.8	6509.33	251603	29094				
1955	683697	36990.7	61157.3	13676.5	449449	55519.1				
2183	44005.1	14592.8	24732.2	5383.15	178302	18633.7				
2605	183464	67525.2	134885	24139.8	913038	123747				

Appendix 5: Integrated GDGT peaks, GDGT ratios and temperatures

	Branched	GDGTs		Standard				
	GDGT-IIIa	GDGT-IIIa'	GDGT-lla	GDGT-IIa'	GDGT-la	C-46		
Stratigraphic position (cm)	1050	1050'	1036	1036'	1022	744	TEX86	BIT
903	0	0	0	0	7506.79	27745.5	0.82	0.019
997	0	0	0	0	5612.77	25676.8	0.85	0.018
1096	0	0	0	0	6685.75	28038.7	0.85	0.017
1215	0	0	0	0	0	32902.8	0.83	0
1280	0	0	0	0	7934.06	26727.2	0.82	0.023
1319	0	0	0	0	0	36135.8	0.85	0
1343	0	0	0	0	7624.03	18558.7	0.82	0.019
1380	0	0	0	0	7552.36	24382.3	0.81	0.028
1405	0	0	0	0	13666.2	43118.1	0.82	0.029
1451	0	0	0	0	12574.5	38346.8	0.78	0.027
1470	0	0	0	0	0	28879.2	0.79	0
1498	0	0	0	0	4479.93	72126.1	0.82	0.005
1548	0	0	0	0	12243.4	30699.5	0.79	0.040
1585	0	0	0	0	9585.4	40402.3	0.79	0.029
1625	0	0	0	0	6346.56	23882.6	0.79	0.023
1706	0	0	0	0	6300.98	38347.7	0.81	0.014
1830	0	0	0	0	2654.63	7793.44	0.81	0.010
1955	0	0	0	0	7607.32	25415.7	0.78	0.017
2183	0	0	0	0	3075.06	8505.44	0.77	0.017
2605	0	0	0	0	10740	41290.1	0.81	0.012

	Kim et al. (2010) Logarithmic	Kim et al. (2010) Linear	Zhang et al. (2011)	Weijers et al. (2011)	Taylor et al. (2013); Hernandez- Sanchez et al. (2014)	Sinninghe Damsté et al. (2012); Blaga et al. (2009)	Pearson et al. (2004)	
			> 0.5 suspicious	5	> 5 suspicious	> 67% suspiciou	ous	
Stratigraphic position (cm)	SST (°C)	SST (°C)	Methane Index	[2]/Cren	[2]/[3]	% [0] vs Cren	Ring Index	
903	32.74	40.32	0.143	0.109	4.717	0.125	3.327	
997	33.66	42.43	0.161	0.135	4.846	0.120	3.326	
1096	33.71	42.54	0.153	0.127	4.739	0.118	3.344	
1215	33.04	40.99	0.162	0.131	4.615	0.134	3.278	
1280	32.83	40.51	0.160	0.123	4.026	0.149	3.237	
1319	33.72	42.56	0.152	0.124	4.521	0.121	3.337	
1343	32.86	40.59	0.155	0.117	3.798	0.135	3.288	
1380	32.38	39.52	0.171	0.130	3.688	0.157	3.196	
1405	32.59	39.99	0.163	0.125	4.036	0.151	3.227	
1451	31.30	37.14	0.173	0.1285	4.217	0.172	3.136	
1470	31.66	37.92	0.166	0.122	4.149	0.172	3.151	
1498	32.85	40.57	0.165	0.129	4.128	0.139	3.260	
1548	31.61	37.81	0.183	0.141	4.414	0.446	2.267	
1585	31.57	37.73	0.183	0.143	4.727	0.180	3.101	
1625	31.69	37.99	0.179	0.137	4.347	0.177	3.117	
1706	32.28	39.30	0.182	0.148	4.956	0.606	1.702	
1830	32.43	39.63	0.162	0.128	4.949	0.145	3.237	
1955	31.17	36.88	0.181	0.136	4.472	0.603	1.707	
2183	30.82	36.12	0.185	0.139	4.594	0.198	3.039	
2605	32.23	39.18	0.179	0.148	5.588	0.167	3.150	

Appendix 6: Fractionation and CO₂ concentrations

Stratigraphic position (cm)	ε _p (‰)	CO ₂ (aq)	CO ₂ (aq) (min)	CO ₂ (aq) (max)	pCO ₂ (ppmv)	pCO ₂ min	pCO ₂ max
903	20.02	23.14	12.18	42.53	958	499	1776
908	20.22	23.87	12.48	44.40	990	513	1858
915	20.02	23.15	12.19	42.54	962	502	1784
925	19.91	22.75	12.02	41.54	947	496	1745
935	19.61	21.77	11.61	39.13	908	480	1648
950	19.61	21.77	11.61	39.12	910	481	1650
950	19.83	22.47	11.90	40.85	941	494	1727
957	19.70	22.06	11.73	39.82	926	488	1687
970	20.13	23.54	12.35	43.53	990	514	1847
985	19.56	21.62	11.54	38.77	911	482	1649
997	19.68	21.98	11.70	39.64	928	489	1689
1004	19.56	21.62	11.54	38.76	913	483	1652
1015	19.78	22.31	11.78	40.80	942	493	1739
1025	19.92	22.78	12.03	41.61	962	503	1773
1041	20.26	24.04	12.55	44.84	1015	525	1911
1052	20.08	23.37	12.28	43.10	987	514	1837
1063	19.61	21.76	11.60	39.10	919	486	1667
1063	20.09	23.39	12.22	43.56	988	512	1857
1080	19.92	22.81	11.98	42.06	964	502	1794
1087	19.10	20.27	10.90	35.83	856	457	1528
1096	19.73	22.15	11.71	40.40	936	490	1723
1105	19.50	21.44	11.41	38.64	905	477	1645
1125	19.87	22.63	11.91	41.59	952	496	1766
1135	20.22	23.88	12.53	44.14	1003	522	1872
1146	20.07	23.33	12.30	42.75	979	511	1810
1165	20.08	23.35	12.31	42.81	978	511	1810
1180	20.13	23.53	12.39	43.26	984	513	1826
1190	19.76	22.26	11.85	40.09	930	490	1690
1200	19.64	21.86	11.68	39.14	912	483	1647
1215	20.05	23.26	12.27	42.58	969	506	1790
1228	19.84	22.51	11.96	40.72	937	493	1710
1240	19.96	22.95	12.14	41.80	954	500	1754
1252	19.92	22.80	12.08	41.43	947	497	1738
1273	20.02	23.15	12.23	42.30	960	502	1771
1280	19.88	22.64	12.01	41.04	939	493	1717
1284	20.14	23.59	12.41	43.42	983	512	1825
1295	19.98	23.02	12.17	41.98	964	505	1774
1310	19.55	21.59	11.57	38.50	908	482	1634
1319	19.92	22.80	12.08	41.42	964	506	1767
1331	20.05	23.27	12.28	42.60	974	509	1800
1343	20.58	25.35	13.13	48.00	1052	540	2010
1354	20.47	24.89	12.86	47.30	1030	527	1975
1369	20.56	25.27	13.01	48.33	1043	532	2013

1. Original CO₂ reconstruction (b-value 100-200; ε_p 25-28%; temperatures reconstructed by TEX₈₆)

1378 20.83 26.46 13.48 51.68 1089 550 2147 1330 20.67 25.74 13.28 49.05 1053 552 2118 1393 20.67 25.74 13.28 49.05 1053 538 2026 1306 20.55 25.22 13.00 48.22 1029 525 1986 1400 20.43 24.70 12.79 46.79 1005 515 1921 1405 20.50 25.00 12.99 47.66 1014 522 1927 1413 20.52 25.10 12.92 47.69 1012 517 1947 1433 20.52 25.10 12.95 47.87 1011 517 1948 1443 20.78 26.22 13.39 51.00 1054 533 2069 1451 20.72 25.94 13.28 50.19 1039 527 2030 1461 20.73 27.36 13.83 54.30 1105 553 2214 1477 20.30 24.21 12.59 45.48 991 510 1879 1488 20.56 25.25 13.09 47.74 1047 538 1999 1508 20.40 24.61 12.83 46.04 1014 524 1914 1515 20.23 20.23 21.24 44.73 979 505 1847 1565 19.29 20.16 $11.$	Stratigraphic position (cm)	ε _p (‰)	CO2(aq)	CO ₂ (aq) (min)	CO ₂ (aq) (max)	pCO ₂ (ppmv)	pCO ₂ min	pCO ₂ max)
1380 20.84 26.48 13.58 51.11 1087 552 2118 1393 20.67 25.74 13.28 49.05 1053 538 2026 1396 20.55 25.22 13.00 48.22 1029 525 1986 1400 20.43 24.70 12.79 46.79 1001 512 1927 1405 20.50 25.00 12.99 47.66 1012 51.7 1947 1413 20.52 25.10 12.95 47.87 1011 51.7 1947 1443 20.72 25.94 13.28 50.19 1039 527 2030 1451 20.72 25.94 13.83 54.30 1105 553 2214 1470 20.02 24.21 12.59 45.8 991 510 1879 1498 20.56 52.52 13.09 47.74 1047 538 1999 1508 20.02 <t< td=""><td>1378</td><td>20.83</td><td>26.46</td><td>13.48</td><td>51.68</td><td>1089</td><td>550</td><td>2147</td></t<>	1378	20.83	26.46	13.48	51.68	1089	550	2147
1393 20.67 25.74 13.28 49.05 1053 538 2026 1396 20.55 25.22 13.00 48.22 1029 525 1986 1400 20.50 25.00 12.99 47.06 1014 522 1927 1418 20.51 25.03 12.92 47.69 1012 517 1947 1433 20.52 25.10 12.95 47.87 1011 517 1948 1443 20.78 26.22 13.39 51.00 1054 533 2069 14451 20.72 25.94 13.28 50.19 1035 527 2030 1461 20.78 26.24 13.48 54.30 1105 553 2214 1477 20.30 24.21 12.59 45.48 991 510 1879 1494 20.56 25.25 13.09 47.74 1047 538 1999 1508 20.40 <t< td=""><td>1380</td><td>20.84</td><td>26.48</td><td>13.58</td><td>51.11</td><td>1087</td><td>552</td><td>2118</td></t<>	1380	20.84	26.48	13.58	51.11	1087	552	2118
1396 20.55 25.22 13.00 48.22 10.29 525 1986 1400 20.43 24.70 12.79 46.79 1005 515 1921 1405 20.50 25.00 12.99 47.66 1012 517 1947 1418 20.51 25.03 12.92 47.69 1012 517 1947 1413 20.52 25.01 12.95 47.87 1011 517 1948 1443 20.72 25.94 13.28 50.19 1039 527 2030 1461 20.72 25.94 13.83 54.30 1005 553 2214 1477 20.30 24.21 12.59 45.48 991 510 1879 1498 20.56 25.25 13.09 47.74 1047 538 1999 1498 20.56 25.25 13.09 47.74 1047 538 1949 1508 19.40 <t< td=""><td>1393</td><td>20.67</td><td>25.74</td><td>13.28</td><td>49.05</td><td>1053</td><td>538</td><td>2026</td></t<>	1393	20.67	25.74	13.28	49.05	1053	538	2026
1400 20.43 24.70 12.79 46.79 1005 515 1921 1405 20.50 25.00 12.99 47.06 1014 522 1927 1418 20.51 25.03 12.92 47.69 1011 517 1947 1433 20.52 25.00 12.95 47.87 1011 517 1948 1443 20.78 26.22 13.39 51.00 1054 533 2069 1451 20.72 25.94 13.28 50.19 1039 527 2030 1461 20.78 26.24 13.40 51.06 1056 534 2073 1470 21.02 27.36 13.83 54.30 1105 553 2214 1477 20.03 24.21 12.29 45.48 991 510 1879 1488 20.56 25.25 13.09 47.74 1047 538 1949 1491 21.63 <td< td=""><td>1396</td><td>20.55</td><td>25.22</td><td>13.00</td><td>48.22</td><td>1029</td><td>525</td><td>1986</td></td<>	1396	20.55	25.22	13.00	48.22	1029	525	1986
1405 20.50 25.00 12.99 47.06 1014 522 1927 1418 20.51 25.03 12.92 47.69 1012 517 1947 1433 20.52 25.10 12.95 47.87 1011 517 1948 1443 20.78 26.22 13.39 50.19 1039 527 2030 1461 20.78 26.24 13.40 51.06 1056 534 2073 1461 20.78 26.24 13.40 51.06 1055 534 2073 1477 20.30 24.21 12.59 45.48 991 510 1879 1448 20.56 25.25 13.09 47.74 1047 538 1999 1508 20.40 24.61 12.83 46.04 1014 544 1914 1515 20.23 23.92 13.16 39.42 887 467 1617 1535 19.67	1400	20.43	24.70	12.79	46.79	1005	515	1921
141820.5125.03 12.92 47.69 1012 517 1947 143320.5225.10 12.95 47.87 1011 517 1948 144320.78 26.22 13.39 51.00 1054 533 2069 145120.72 25.94 13.28 50.19 1039 527 2030 1461 20.78 26.24 13.40 51.06 1056 534 2073 1470 21.02 27.36 13.38 54.30 1105 553 2214 1477 20.30 24.21 12.59 45.48 991 510 1879 1498 20.56 25.25 13.09 47.74 1047 538 1999 1508 20.40 24.61 12.83 46.04 1014 524 1914 1515 20.23 23.92 12.47 44.73 979 505 1847 1536 19.63 21.83 11.66 39.42 887 467 1617 1548 19.67 21.96 11.66 39.42 887 466 1619 1555 20.17 23.70 12.38 44.15 956 495 1798 1565 19.29 20.81 11.17 36.98 839 446 1505 1578 18.87 19.66 10.67 34.31 793 426 1336 1585 19.42 21.19 11.33 37.88 855 453 </td <td>1405</td> <td>20.50</td> <td>25.00</td> <td>12.99</td> <td>47.06</td> <td>1014</td> <td>522</td> <td>1927</td>	1405	20.50	25.00	12.99	47.06	1014	522	1927
1433 20.52 25.10 12.95 47.87 1011 517 1948 1443 20.78 26.22 13.39 51.00 1054 533 2069 1451 20.72 25.94 13.28 50.19 1039 527 2030 1461 20.78 26.24 13.40 51.06 1056 534 2073 1470 21.02 27.36 13.83 54.30 1105 553 2214 1477 20.30 24.21 12.59 45.48 991 510 1879 1498 20.56 25.25 13.09 47.74 1047 538 1999 1508 20.40 24.61 12.83 46.04 1014 524 1914 1515 20.23 23.92 12.47 44.73 979 505 1847 1515 20.17 23.70 12.38 44.15 966 1617 1515 19.67 24.91 11.33 37.88 839 446 1505 15178 18.87	1418	20.51	25.03	12.92	47.69	1012	517	1947
1443 20.78 26.22 13.39 51.00 1054 533 2069 1451 20.72 25.94 13.28 50.19 1039 527 2030 1461 20.78 26.24 13.40 51.06 1056 534 2073 1470 21.02 27.36 13.83 54.30 1105 553 2214 1477 20.30 24.21 12.59 45.48 991 510 1879 1488 20.56 25.25 13.09 47.74 1047 538 1914 1508 20.40 24.61 12.83 46.04 1014 524 1914 1515 20.23 23.92 12.47 44.73 979 505 1847 1515 20.17 23.70 11.66 39.74 886 466 1619 1555 20.17 23.70 11.33 37.78 823 442 1505 1565 19.29 21	1433	20.52	25.10	12.95	47.87	1011	517	1948
145120.7225.9413.2850.1910395272030146120.7826.2413.4051.0610565342073147021.0227.3613.8354.3011055532214147720.3024.2112.5945.489915101879149820.5625.2513.0947.7410475381999150820.4024.6112.8346.0410145241914151520.2323.9212.4744.739795051847153619.6321.8311.6039.4288746671617154819.6721.9611.6639.748864661619155520.1723.7012.3844.159564951798156519.2920.8111.1736.988394461505157818.8719.6610.6734.317934261336157819.4121.1511.3337.888554531542159119.4221.911.3337.888554531542159519.6621.9211.6439.648864661617160519.5921.7011.5539.108804641617161719.0120.3311.0135.5383344515791615219.6521.9211.6439.64	1443	20.78	26.22	13.39	51.00	1054	533	2069
1461 20.78 26.24 13.40 51.06 1056 534 2073 1470 21.02 27.36 13.83 54.30 1105 553 2214 1477 20.30 24.21 12.59 45.48 991 510 1879 1498 20.56 25.25 13.09 47.74 1047 538 1999 1508 20.40 24.61 12.83 46.04 1014 524 1914 1515 20.23 23.92 12.47 44.73 979 505 1847 1536 19.63 21.83 11.60 39.42 887 466 1619 1555 20.17 23.70 12.38 44.15 956 495 1798 1555 19.29 20.81 11.17 36.98 839 446 1505 1578 18.87 19.66 10.67 34.31 793 426 1396 1578 19.42 21.19 11.33 37.88 855 453 1542 1597 19.42 21.19 11.33 37.88 855 453 1542 1597 19.66 21.92 11.64 39.64 866 61617 1605 19.59 21.70 11.55 39.10 886 466 1617 1652 19.66 21.92 11.64 39.64 866 4616 1671 1652 19.66 21.92 11.65 39.10 </td <td>1451</td> <td>20.72</td> <td>25.94</td> <td>13.28</td> <td>50.19</td> <td>1039</td> <td>527</td> <td>2030</td>	1451	20.72	25.94	13.28	50.19	1039	527	2030
1470 21.02 27.36 13.83 54.30 1105 553 2214 1477 20.30 24.21 12.59 45.48 991 510 1879 1498 20.56 25.25 13.09 47.74 1047 538 1999 1508 20.40 24.61 12.83 46.04 1014 524 1914 1515 20.23 23.92 12.47 44.73 979 505 1847 1536 19.63 21.83 11.60 39.42 887 467 1617 1548 19.67 21.96 11.66 39.74 886 466 1619 1555 20.17 23.70 12.38 44.15 956 495 1798 1565 19.29 20.81 11.17 36.98 839 446 1505 1578 18.87 19.66 10.67 34.31 793 426 1396 1585 19.41 21.15 11.31 37.78 855 453 1542 1597 19.46 21.92 11.64 39.64 886 466 1617 1655 19.59 21.70 11.55 39.10 880 464 1601 1652 19.66 21.92 11.64 39.64 886 466 1617 1655 19.59 21.70 11.55 39.10 880 464 1601 1652 19.59 21.70 11.55 <t< td=""><td>1461</td><td>20.78</td><td>26.24</td><td>13.40</td><td>51.06</td><td>1056</td><td>534</td><td>2073</td></t<>	1461	20.78	26.24	13.40	51.06	1056	534	2073
1477 20.30 24.21 12.59 45.48 991 510 1879 1498 20.56 25.25 13.09 47.74 1047 538 1999 1508 20.40 24.61 12.83 46.04 1014 524 1914 1515 20.23 23.92 12.47 44.73 979 505 1847 1536 19.63 21.83 11.60 39.42 887 467 1617 1548 19.67 21.96 11.66 39.74 886 466 1619 1555 20.17 23.70 12.38 44.15 956 495 1798 1565 19.29 20.81 11.17 36.98 839 446 1505 1578 18.87 19.66 10.67 34.31 793 4256 1396 1585 19.41 21.15 11.31 37.78 855 453 1542 1597 19.16 20.44 11.01 36.11 825 440 1471 1605 19.54 21.54 11.48 38.72 870 459 1579 1625 19.66 21.92 11.64 39.64 886 466 1617 1652 19.59 21.70 11.55 39.10 880 464 1601 1652 19.59 21.70 11.55 39.10 880 464 1601 1652 19.59 21.70 11.55 <t< td=""><td>1470</td><td>21.02</td><td>27.36</td><td>13.83</td><td>54.30</td><td>1105</td><td>553</td><td>2214</td></t<>	1470	21.02	27.36	13.83	54.30	1105	553	2214
149820.5625.2513.0947.7410475381999150820.4024.6112.8346.0410145241914151520.2323.9212.4744.739795051847153619.6321.8311.6039.428874671617154819.6721.9611.6639.748864661619155520.1723.7012.3844.159564951798155519.2920.8111.1736.988394461505157818.8719.6610.6734.317934261396158519.4121.1511.3137.788524521537159119.4221.1911.3337.888554531542159719.1620.4411.0136.118254401471160519.5421.5411.4838.728704591579162519.6621.9211.6439.648864661617165219.921.7011.5539.108804641601167219.0120.0310.8335.148154361443169319.1220.3311.0135.538304451464169319.1220.3311.0135.538334461587172919.1020.2810.9435.72831 </td <td>1477</td> <td>20.30</td> <td>24.21</td> <td>12.59</td> <td>45.48</td> <td>991</td> <td>510</td> <td>1879</td>	1477	20.30	24.21	12.59	45.48	991	510	1879
1508 20.40 24.61 12.83 46.04 1014 524 1914 1515 20.23 23.92 12.47 44.73 979 505 1847 1536 19.63 21.83 11.60 39.42 887 467 1617 1548 19.67 21.96 11.66 39.74 886 466 1619 1555 20.17 23.70 12.38 44.15 956 495 1798 1565 19.29 20.81 11.17 36.98 839 446 1505 1578 18.87 19.66 10.67 34.31 793 426 1396 1585 19.41 21.15 11.31 37.78 852 452 1337 1591 19.42 21.19 11.33 37.88 855 453 1542 1597 19.16 20.44 11.01 36.11 825 440 1471 1605 19.54 21.54 11.48 38.72 870 459 1579 1625 19.66 21.92 11.64 39.64 886 466 1617 1652 19.59 21.70 11.55 39.10 880 464 1601 1672 19.01 20.03 10.83 35.14 815 436 1443 1693 19.12 20.33 11.01 35.53 830 445 1464 1706 19.54 21.55 11.55	1498	20.56	25.25	13.09	47.74	1047	538	1999
1515 20.23 23.92 12.47 44.73 979 505 1847 1536 19.63 21.83 11.60 39.42 887 467 1617 1548 19.67 21.96 11.66 39.74 886 466 1619 1555 20.17 23.70 12.38 44.15 956 495 1798 1565 19.29 20.81 11.17 36.98 839 446 1505 1578 18.87 19.66 10.67 34.31 793 426 1396 1585 19.41 21.15 11.31 37.78 852 452 1537 1591 19.42 21.19 11.33 37.88 855 453 1542 1597 19.16 20.44 11.01 36.11 825 440 1471 1605 19.54 21.54 11.48 38.72 870 459 1579 1625 19.66 21.92 11.64 39.64 886 466 1617 1652 19.59 21.70 11.55 39.10 880 464 1601 1672 19.01 20.03 10.83 35.14 815 436 1443 1693 19.12 20.33 11.01 35.53 830 445 1464 1706 19.54 21.55 11.55 38.38 883 468 1587 1729 19.10 20.28 10.94	1508	20.40	24.61	12.83	46.04	1014	524	1914
153619.63 21.83 11.60 39.42 887 467 1617 154819.67 21.96 11.66 39.74 886 466 1619 1555 20.17 23.70 12.38 44.15 956 495 1798 1565 19.29 20.81 11.17 36.98 839 446 1505 1578 18.87 19.66 10.67 34.31 793 426 1396 1585 19.41 21.15 11.31 37.78 852 452 1537 1591 19.42 21.19 11.33 37.88 855 453 1542 1597 19.16 20.44 11.01 36.11 825 440 1471 1605 19.54 21.54 11.48 38.72 870 459 1579 1625 19.66 21.92 11.64 39.64 886 466 1617 1652 19.59 21.70 11.55 39.10 880 464 1601 1672 19.01 20.03 10.83 35.14 815 436 1443 1693 19.12 20.33 11.01 35.53 830 445 1464 1706 19.54 21.55 11.55 38.38 883 468 1587 1729 19.10 20.28 10.94 35.72 831 444 1478 1729 19.46 21.30 11.38 38.14 875 463 </td <td>1515</td> <td>20.23</td> <td>23.92</td> <td>12.47</td> <td>44.73</td> <td>979</td> <td>505</td> <td>1847</td>	1515	20.23	23.92	12.47	44.73	979	505	1847
154819.6721.9611.6639.748864661619155520.1723.7012.3844.159564951798156519.2920.8111.1736.988394461505157818.8719.6610.6734.317934261396158519.4121.1511.3137.788524521537159119.4221.1911.3337.888554531542159719.1620.4411.0136.118254401471160519.5421.5411.4838.728704591579162519.6621.9211.6439.648864661617165219.5921.7011.5539.108804441601167219.0120.0310.8335.148154361443169319.1220.3311.0135.538304451464170619.5421.5511.5538.388834681587172919.1020.2810.9435.728314441478174920.0623.2912.2143.089554961784178219.4621.3011.3838.148754631581183020.2624.0312.5245.009875091867186540.7840.7640.6740.6760.784	1536	19.63	21.83	11.60	39.42	887	467	1617
155520.1723.7012.3844.159564951798156519.2920.8111.1736.988394461505157818.8719.6610.6734.317934261396158519.4121.1511.3137.788524521537159119.4221.1911.3337.888554531542159719.1620.4411.0136.118254401471160519.5421.5411.4838.728704591579162519.6621.9211.6439.648864661617165219.5921.7011.5539.108804641601167219.0120.0310.8335.148154361443169319.1220.3311.0135.538304451464170619.5421.5511.5538.388834681587172919.1020.2810.9435.728314441478174920.0623.2912.2143.089554961784178219.4621.3011.3838.148754631581183020.2624.0312.5245.009875091867	1548	19.67	21.96	11.66	39.74	886	466	1619
156519.2920.8111.1736.988394461505157818.8719.6610.6734.317934261396158519.4121.1511.3137.788524521537159119.4221.1911.3337.888554531542159719.1620.4411.0136.118254401471160519.5421.5411.4838.728704591579162519.6621.9211.6439.648864661617165219.5921.7011.5539.108804641601167219.0120.0310.8335.148154361443169319.1220.3311.0135.538304451464170619.5421.5511.5538.388834681587172919.1020.2810.9435.728314441478174920.0623.2912.2143.089554961784178219.4621.3011.3838.148754631581183020.2624.0312.5245.009875091867	1555	20.17	23.70	12.38	44.15	956	495	1798
157818.8719.6610.6734.317934261396158519.4121.1511.3137.788524521537159119.4221.1911.3337.888554531542159719.1620.4411.0136.118254401471160519.5421.5411.4838.728704591579162519.6621.9211.6439.648864661617165219.5921.7011.5539.108804641601167219.0120.0310.8335.148154361443169319.1220.3311.0135.538304451464170619.5421.5511.5538.388834681587172919.1020.2810.9435.728314441478174920.0623.2912.2143.089554961784178219.4621.3011.3838.148754631581183020.2624.0312.5245.009875091867	1565	19.29	20.81	11.17	36.98	839	446	1505
158519.4121.1511.3137.788524521537159119.4221.1911.3337.888554531542159719.1620.4411.0136.118254401471160519.5421.5411.4838.728704591579162519.6621.9211.6439.648864661617165219.5921.7011.5539.108804641601167219.0120.0310.8335.148154361443169319.1220.3311.0135.538304451464170619.5421.5511.5538.388834681587172919.1020.2810.9435.728314441478174920.0623.2912.2143.089554961784178219.4621.3011.3838.148754631581183020.2624.0312.5245.009875091867	1578	18.87	19.66	10.67	34.31	793	426	1396
159119.4221.1911.3337.888554531542159719.1620.4411.0136.118254401471160519.5421.5411.4838.728704591579162519.6621.9211.6439.648864661617165219.5921.7011.5539.108804641601167219.0120.0310.8335.148154361443169319.1220.3311.0135.538304451464170619.5421.5511.5538.388834681587172919.1020.2810.9435.728314441478174920.0623.2912.2143.089554961784178219.4621.3011.3838.148754631581183020.2624.0312.5245.009875091867	1585	19.41	21.15	11.31	37.78	852	452	1537
159719.1620.4411.0136.118254401471160519.5421.5411.4838.728704591579162519.6621.9211.6439.648864661617165219.5921.7011.5539.108804641601167219.0120.0310.8335.148154361443169319.1220.3311.0135.538304451464170619.5421.5511.5538.388834681587172919.1020.2810.9435.728314441478174920.0623.2912.2143.089554961784178219.4621.3011.3838.148754631581183020.2624.0312.5245.009875091867	1591	19.42	21.19	11.33	37.88	855	453	1542
160519.5421.5411.4838.728704591579162519.6621.9211.6439.648864661617165219.5921.7011.5539.108804641601167219.0120.0310.8335.148154361443169319.1220.3311.0135.538304451464170619.5421.5511.5538.388834681587172919.1020.2810.9435.728314441478174920.0623.2912.2143.089554961784178219.4621.3011.3838.148754631581183020.2624.0312.5245.009875091867	1597	19.16	20.44	11.01	36.11	825	440	1471
162519.6621.9211.6439.648864661617165219.5921.7011.5539.108804641601167219.0120.0310.8335.148154361443169319.1220.3311.0135.538304451464170619.5421.5511.5538.388834681587172919.1020.2810.9435.728314441478174920.0623.2912.2143.089554961784178219.4621.3011.3838.148754631581183020.2624.0312.5245.009875091867	1605	19.54	21.54	11.48	38.72	870	459	1579
165219.5921.7011.5539.108804641601167219.0120.0310.8335.148154361443169319.1220.3311.0135.538304451464170619.5421.5511.5538.388834681587172919.1020.2810.9435.728314441478174920.0623.2912.2143.089554961784178219.4621.3011.3838.148754631581183020.2624.0312.5245.009875091867	1625	19.66	21.92	11.64	39.64	886	466	1617
167219.0120.0310.8335.148154361443169319.1220.3311.0135.538304451464170619.5421.5511.5538.388834681587172919.1020.2810.9435.728314441478174920.0623.2912.2143.089554961784178219.4621.3011.3838.148754631581183020.2624.0312.5245.009875091867	1652	19.59	21.70	11.55	39.10	880	464	1601
169319.1220.3311.0135.538304451464170619.5421.5511.5538.388834681587172919.1020.2810.9435.728314441478174920.0623.2912.2143.089554961784178219.4621.3011.3838.148754631581183020.2624.0312.5245.009875091867	1672	19.01	20.03	10.83	35.14	815	436	1443
170619.5421.5511.5538.388834681587172919.1020.2810.9435.728314441478174920.0623.2912.2143.089554961784178219.4621.3011.3838.148754631581183020.2624.0312.5245.009875091867	1693	19.12	20.33	11.01	35.53	830	445	1464
172919.1020.2810.9435.728314441478174920.0623.2912.2143.089554961784178219.4621.3011.3838.148754631581183020.2624.0312.5245.009875091867186510.7823.2311.9240.672144701675	1706	19.54	21.55	11.55	38.38	883	468	1587
1749 20.06 23.29 12.21 43.08 955 496 1784 1782 19.46 21.30 11.38 38.14 875 463 1581 1830 20.26 24.03 12.52 45.00 987 509 1867 1865 10.78 23.23 11.92 40.67 911 470 1675	1729	19.10	20.28	10.94	35.72	831	444	1478
1782 19.46 21.30 11.38 38.14 875 463 1581 1830 20.26 24.03 12.52 45.00 987 509 1867 1865 10.78 23.23 11.92 40.67 011 470 1675	1749	20.06	23.29	12.21	43.08	955	496	1784
1830 20.26 24.03 12.52 45.00 987 509 1867 1865 10.78 23.23 11.92 40.67 011 170 1675	1782	19.46	21.30	11.38	38.14	875	463	1581
	1830	20.26	24.03	12.52	45.00	987	509	1867
10/5 12/10/2013 12/2013 12/2014 12/2014 12/2014 12/2014 12/2014 12/2014 12/2014 12/2014 12/2014 12/2014 12/2014	1865	19.78	22.33	11.82	40.67	911	478	1675
1891 19.92 22.78 12.00 41.80 923 482 1710	1891	19.92	22.78	12.00	41.80	923	482	1710
1935 19.80 22.40 11.84 40.82 901 472 1658	1935	19.80	22.40	11.84	40.82	901	472	1658
1955 18.43 18.58 10.18 31.86 742 403 1285	1955	18.43	18.58	10.18	31.86	742	403	1285
1980 19.94 22.88 12.10 41.69 913 478 1680	1980	19.94	22.88	12.10	41.69	913	478	1680
2015 19.38 21.06 11.32 37.29 840 447 1501	2015	19.38	21.06	11.32	37.29	840	447	1501
2050 19.46 21.30 11.43 37.87 848 451 1523	2050	19.46	21.30	11.43	37.87	848	451	1523
2138 20.07 23.35 12.30 42.86 927 483 1718	2138	20.07	23.35	12.30	42.86	927	483	1718
2183 19.99 23.04 12.17 42.10 913 477 1684	2183	19.99	23.04	12.17	42.10	913	477	1684

Stratigraphic position (cm)	εр (‰)	CO2(aq)	CO2(aq) (min)	CO2(aq) (max)	pCO2	pCO2 (min)	pCO2 (max)
2201	20.38	24.49	12.77	45.82	973	503	1839
2223	20.07	23.32	12.28	42.79	930	485	1722
2248	19.92	22.79	12.06	41.48	911	478	1675
2273	20.03	23.19	12.23	42.46	930	486	1719
2293	20.11	23.48	12.35	43.20	945	492	1755
2343	19.59	21.72	11.61	38.86	877	464	1583
2380	20.16	23.68	12.43	43.70	958	499	1786
2455	20.07	23.35	12.30	42.86	948	495	1757
2520	20.12	23.52	12.37	43.32	958	499	1781
2605	20.69	25.82	13.30	49.37	1055	538	2036

2. CO_2 reconstruction with constant ε_f (25‰)

Stratigraphic position (cm)	pCO ₂ (ppmv)	pCO ₂ min	pCO ₂ max	Strat. pos. (cm)	pCO ₂ (ppmv)	pCO ₂ min	pCO ₂ max
903	1246	787	1776	1405	1352	855	1927
908	1300	820	1858	1418	1350	845	1947
915	1252	791	1784	1433	1350	845	1948
925	1226	775	1745	1443	1428	891	2069
935	1161	736	1648	1451	1403	876	2030
950	1163	737	1650	1461	1431	893	2073
950	1214	768	1727	1470	1521	946	2214
957	1188	752	1687	1477	1307	820	1879
970	1295	817	1847	1498	1401	886	1999
985	1163	737	1649	1508	1345	851	1914
997	1190	754	1689	1515	1286	808	1847
1004	1165	738	1652	1536	1134	716	1617
1015	1213	762	1739	1548	1135	716	1619
1025	1246	788	1773	1555	1253	787	1798
1041	1337	843	1911	1565	1060	671	1505
1052	1288	813	1837	1578	987	626	1396
1063	1175	745	1667	1585	1081	684	1537
1063	1290	808	1857	1591	1085	686	1542
1080	1249	783	1794	1597	1037	657	1471
1087	1074	679	1528	1605	1109	701	1579
1096	1203	756	1723	1625	1134	716	1617
1105	1152	725	1645	1652	1124	710	1601
1125	1231	772	1766	1672	1019	646	1443
1135	1318	836	1872	1693	1041	665	1464
1146	1277	810	1810	1706	1125	717	1587
1165	1276	810	1810	1729	1043	661	1478
1180	1287	81/	1826	1/49	1246	/83	1/84
1190	1196	761	1690	1/82	1111	/03	1581
1200	1167	743	1647	1830	1300	816	1867
1215	1262	801	1790	1865	11/3	740	10/5
1228	1209	709	1710	1891	1190	753	1/10
1240	1239	787	1734	1935	011	732	1000
1232	1227	700	1750	1955	911	56U 751	1205
1273	1230	794	1717	2015	1164	677	1000
1280	1213	916	1925	2013	1004	686	1501
1204	1260	705	1023	2030	1078	766	1710
1255	1150	738	163/	2138	1186	752	168/
1310	1248	793	1767	2185	1289	815	1839
1315	1240	806	1800	2201	1203	768	1722
1343	1409	890	2010	2223	1181	749	1675
1343	1371	859	1975	2248	1211	767	1719
1354	1395	873	2013	2273	1235	782	1755
1305	1481	923	2013	2255	1120	712	1583
1380	1479	932	2118	2340	1256	795	1786
1300	1418	895	2026	2300	1230	784	1757
1396	1376	861	1986	2520	1253	794	1781
1400	1334	836	1921	2605	1422	896	2036

Stratigraphic position (cm)	pCO ₂ (ppmv)	pCO ₂ min	pCO₂max	Strat. pos. (cm)	pCO ₂ (ppmv)	pCO ₂ min	pCO ₂ max
903	854	450	1556	1405	1113	567	2157
908	878	460	1615	1418	1118	565	2197
915	852	449	1549	1433	1124	568	2216
925	836	443	1512	1443	1181	590	2384
935	801	427	1427	1451	1172	586	2354
950	800	427	1424	1461	1181	590	2384
950	823	437	1479	1470	1229	608	2532
957	807	430	1441	1477	1067	545	2053
970	856	451	1561	1498	1100	562	2121
985	790	422	1400	1508	1079	554	2062
997	801	427	1426	1515	1054	540	2019
1004	788	422	1397	1536	820	435	1478
1015	812	430	1464	1548	829	438	1500
1025	828	439	1490	1555	893	465	1660
1041	870	457	1595	1565	787	421	1400
1052	847	447	1539	1578	745	402	1303
1063	/93	424	1408	1585	800	426	1430
1063	848	445	1553	1591	801	426	1433
1080	828	437	1504	1597	//3	414	1367
1087	741	399	1299	1605	813	432	1461
1105	008 207	427	1450	1652	820	437	1493
1105	702 925	417	1/06	1672	754	455	1202
1125	860	450	1490	1602	754	400	1322
1135	803	450	1539	1095	804	412	1478
1165	853	451	1543	1729	758	408	1333
1180	860	454	1561	1749	866	454	1590
1190	817	436	1458	1782	794	423	1416
1200	804	430	1428	1830	890	464	1653
1215	854	451	1546	1865	835	441	1515
1228	828	440	1485	1891	856	450	1567
1240	844	447	1522	1935	847	446	1544
1252	840	445	1511	1955	709	386	1222
1273	853	451	1543	1980	871	458	1590
1280	835	444	1502	2015	803	429	1428
1284	865	456	1574	2050	813	434	1451
1295	842	446	1517	2138	892	467	1643
1310	790	424	1394	2183	882	463	1618
1319	828	440	1483	2201	934	484	1751
1331	850	450	1537	2223	888	465	1632
1343	1104	564	2132	2248	866	456	1578
1354	1087	553	2108	2273	878	461	1609
1369	1106	561	2164	2293	887	465	1630
1378	1164	583	2330	2343	820	437	1467
1380	1168	588	2313	2380	889	466	1637
1393	1137	577	2225	2455	875	460	1601
1396	1117	565	2194	2520	879	462	1611
1400	1096	557	2134	2605	959	494	1816

3. CO_2 reconstruction with temperature increase (30 °C to 34 °C during MECO)

4. CO₂ reconstruction with temperature increase (b-increase of 30)

Stratigraphic position (cm)	pCO ₂ (ppmv)	pCO ₂ min	pCO ₂ max	Strat. pos. (cm)	pCO ₂ (ppmv)	pCO ₂ min	pCO ₂ max
903	958	499	1776	1405	1216	678	2216
908	990	513	1858	1418	1214	673	2239
915	962	502	1784	1433	1214	672	2240
925	947	496	1745	1443	1264	693	2379
935	908	480	1648	1451	1247	685	2335
950	910	481	1650	1461	1267	694	2384
950	941	494	1727	1470	1326	719	2546
957	926	488	1687	1477	1189	664	2161
970	990	514	1847	1498	1257	699	2298
985	911	482	1649	1508	1216	681	2201
997	928	489	1689	1515	1174	657	2124
1004	913	483	1652	1536	1064	607	1859
1015	942	493	1739	1548	886	466	1619
1025	962	503	1773	1555	956	495	1798
1041	1015	525	1911	1565	839	446	1505
1052	987	514	1837	1578	793	426	1396
1063	919	486	1667	1585	852	452	1537
1063	988	512	1857	1591	855	453	1542
1080	964	502	1794	1597	825	440	1471
1087	856	457	1528	1605	870	459	1579
1096	936	490	1723	1625	886	466	1617
1105	905	477	1645	1652	880	464	1601
1125	952	496	1766	1672	815	436	1443
1135	1003	522	1872	1693	830	445	1464
1146	979	511	1810	1706	883	468	1587
1165	978	511	1810	1729	831	444	1478
1180	984	513	1826	1749	955	496	1784
1190	930	490	1690	1782	875	463	1581
1200	912	483	1647	1830	987	509	1867
1215	969	506	1790	1865	911	478	1675
1228	937	493	1710	1891	923	482	1710
1240	954	500	1754	1935	901	472	1658
1252	947	497	1738	1955	742	403	1285
1273	960	502	1771	1980	913	478	1680
1280	939	493	1717	2015	840	447	1501
1284	983	512	1825	2050	848	451	1523
1295	964	505	1774	2138	927	483	1718
1310	908	482	1634	2183	913	477	1684
1319	964	506	1767	2201	973	503	1839
1331	974	509	1800	2223	930	485	1722
1343	1262	701	2311	2248	911	478	1675
1354	1236	685	2272	2273	930	486	1719
1369	1251	692	2315	2293	945	492	1755
1378	1307	715	2469	2343	877	464	1583
1380	1304	718	2436	2380	958	499	1786
1393	1264	700	2330	2455	948	495	1757
1396	1235	683	2284	2520	958	499	1781
1400	1206	670	2209	2605	1055	538	2036

Appendix 7: Ketone chromatographs



GC chromatograph of ketone fraction, BX170 (1215 cm)



GC chromatograph of apolar-lipid fraction, BX196 (1470 cm)

Appendix 8: Apolar-lipid chromatographs



GC chromatograph of apolar-lipid fraction, BX170 (1215 cm)



GC chromatograph of apolar-lipid fraction, BX196 (1470 cm)