Scientific Report

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Proposal Title: Application for a Short Visit Grant to attend the Urbino Summer School in Paleoclimatology 2014.

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1 Aim and Purpose of this visit

The main topic of the Urbino Summer School of Paleoclimatology (USSP) 2014 was the reconstruction of past climate dynamics using data and models. With the uses of different marine and terrestrial proxies it is possible to conclude the evolution of ocean currents, carbon and climate cycles and the response mechanisms between the individual spheres of the Earth and their extent and change over time. The analysis of former climates like the hothouse conditions during the Paleogene can help to improve predictions about the future of climate. Within the scope of the USSP, we focused on proxies, the long-term carbon cycle and cyclostratigraphy. Through lectures, practicals and field trips we enhanced our knowledge about paleobiological and geochemical proxies and applied our knowledge to understand the dynamics of hyperthermals, OAEs and climate cycles. The purpose of my visit was to get a condensed introduction into this topics. As I just started my PhD at the MARUM Centre for Marine Environmental Sciences the obtained knowledge ensures a strong basis for a successful PhD project.

2 Description of the work carried out during the visit

The USSP was splitted into lectures, a field trip and practicals.

2.1 Lectures

In total, we had 48 lectures of 90 minutes each. During the first days we talked about the basics of the carbon cycle, marine life, stable isotope measurements and other terrestrial and marine, biotic and inorganic proxies whereas the second half was centered around several case studies from the Cenozoic and Mesozoic. Due to the limited length of this report I will cover only several selected topics which were the most important for me particularly with an eye to my own PhD project.

2.1.1 Proxies

An important example of widely used proxies are the ratios of stable isotopes, types of particular elements with the same atomic number Z, but a different quantity of neutrons. Stable isotope ratios are important proxies for the reconstruction of paleo conditions because they are directly regulated by a change in these same conditions. Oxygen isotopes, for example, are being used for the calculation of paleotemperature (Epstein et al., 1953). Oxygen has three stable isotopes, ^{16}O, ^{17}O and ^{18}O. ^{16}O and ^{18}O are most common and their ratio can be identified using mass spectroscopy. Stable isotope ratios are altered by isotope fractionation, that being the change in the ratio of particular isotopes by a isotope discrimination due to the difference of the reaction rates of the individual isotopes.

Stable oxygen isotopes are being described by $\delta^{18}O$, a measure of the ratio of stable oxygen isotopes, defined by:

$$\delta^{18}O(\ ^o\!/_{oo}) = \left(\frac{\left(\frac{^{18}O}{^{16}O}\right)_{\text{sample}} - \left(\frac{^{18}O}{^{16}O}\right)_{\text{standard}}}{\left(\frac{^{18}O}{^{16}O}\right)_{\text{standard}}} \right) \cdot 1000$$

respectively

$$\delta^{18}O(\ ^o\!/_{oo}) = \left(\frac{\left(\frac{^{18}O}{^{16}O}\right)_{\text{sample}}}{\left(\frac{^{18}O}{^{16}O}\right)_{\text{standard}}} - 1 \right) \cdot 1000,$$

where the standard is a reference sample with a known isotope ratio, that being VSMOW (Vienna Standard Mean Ocean Water) with $\frac{^{18}O}{^{16}O}$ of $2005.20 \pm 0.43\ ppm$. During evaporation, sea water gets depleted in the lighter ^{16}O-isotope because H_2O with ^{16}O-isotopes tends to evaporate faster because of its lower mass and thus higher vibrational frequency. $\delta^{18}O$ of the sea water becomes higher, $\delta^{18}O$ of the water vapour becomes lower since it is enriched with the lighter isotope. When moving to higher latitudes and cooler air masses the water vapour in the moist air mass condenses and is thus depleted in ^{18}O, described by the Rayleigh Distillation (see e.g. (Bigeleisen & Wolfsberg, 1958):

$$R_v = R_f^0 f^{\alpha - 1},$$

where R_v is the isotope ratio of remaining vapor, R_f^0 is the isotope ratio in initial vapor and f is the fraction of vapor remaining where α is the fractionation factor typical for the particular process (~ 1.009 for the condensation of liquid water from vapour). The water vapour condensing and raining out at high latitudes is enriched in ^{16}O that gets trapped in ice shields. This leads to low $\delta^{18}O$-values during glacials that can be recognized in ice cores. On the opposite, fossil shells (foraminifera etc.) become enriched in heavier isotopes due to the higher $\delta^{18}O$-values in the sea water. During interglacials the ice shields melt and water enriched with lighter isotopes returns to the ocean and lowers $\delta^{18}O$-values.

This dependence between evaporation (and therefore temperature) and $\delta^{18}O$ can be used to calculate a paleo temperature (experimentally determined by (McCrea, 1950)):

$$T(^oC) = 16.0 - 5.17(\delta_c - \delta_w) + 0.092(\delta_c - \delta_w)^2,$$

with δ_c = the isotope ratio of the carbonate and δ_w = the isotope ratio of the sorrounding water.

There are useful rules of thumb for the change of palaeo temperature: At $0\,^\circ$C, $1\,^\circ$C change in temperature equals a $0.25\,^o/_{oo}$-change in δ^{18}O, at $30\,^\circ$C, $1\,^\circ$C change in temperature equals a $0.2\,^o/_{oo}$-change in δ^{18}O.

Carbon isotopes Carbon has two stable isotopes, ^{12}C and ^{13}C which are put into relation using δ^{13}C, similar to oxygen isotopes. Carbon can be measured within calcareous shells of microfossils or organic matter. But it must be considered that the isotope ratios of organic compounds can be skewed by vital effects. Plants discriminate the isotopic composition during the photosynthesis depending on the water stress, as response to light or whether the plant is a C_3- or a C_4-plant.

Due to thermodynamic properties, phytoplankton tends to incorporate ^{12}C more likely. A shift to lower δ^{13}C-values reflects an enrichment of CO_2 in sea water and due to Henry's law [1] an increase of atmospheric CO_2. The identification of the partial pressure of CO_2 in the past (paleobarometer) is useful to reconstruct global temperature or the amount of acidification within the ocean and thus, the dissolution of carbonate.

Carbon isotopes are an useful way to reconstruct former periods of excessive warmth like hyperthermals with an supposed enhanced input of CO_2.

Organic compounds Another proxy which is important to mention is the TEX_{86}-Index. For this purpose, total glycerol dialkyl glycerol tetraethers (GDGTs, glycerides formed via ether linkages) of membrane lipids of Thaumarchaeota, a marine phylum of archaea, are analysed for their ratio of different types of GDGTs which differ in the number of cyclopentan or -hexan moieties. The abundance of the indicidual GDGTs is dependent on the temperature. The TEX_{86}-Index was defined by (Schouten et al., 2002) as

$$TEX_{86} = \frac{GDGT_{IV} + GDGT_V + GDGT_{VI}}{GDGT_{III} + GDGT_{IV} + GDGT_V + GDGT_{VI}}$$

with the index defined as the number of cyclopentan rings minus 1. $GDGT_V$ has three cyclopentan rings plus one cyclohexan ring. $GDGT_{VI}$ is a stereoisomer of $GDGT_V$. The TEX_{86}-Index of core-top material is best correlated with mean annual sea surface temperature (SST):

$$SST = 56.2 \times TEX_{86} - 10.78$$

The $U^{k'}_{37}$-Index can also be used for SST-reconstruction. It takes advantage of the abundance of alkenones, highly resistant ketones existent in several

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[1]Henry's law describes the proportionality of the concentration of a given gas in a given volume of liquid to the partial pressure of the gas above the liquid. It is defined as $p = k_h c$, p = partial pressure of a gaseous phase above a solution, c = concentration of the dissolved gas and k_h = a constant with the dimension of pressure divided by concentration.

coccolithophores like *Emiliania huxleyi* which are distinguished by the number of carbon atoms in the molecule and the amount of saturation (either doubly or triply unsaturated). The $U_{37}^{k'}$-Index is given by:

$$U_{37}^{k'} = \frac{[C_{37:2}]}{[C_{37:2} + C_{37:3}]}$$

and the SST is calculated as:

$$SST = 29.41 \times U_{37}^{k'} - 1.15,$$

which means that the index can not be used for temperatures above approx. 28.2 degrees celsius. Additionaly, there are other control mechanisms which cause a prominent shift in the distribution of alkenones, that is, a limitation of nutrients which lowers the $U_{37}^{k'}$-Index or for example the limitation of light which raises it. Another relevant factor might be diagenesis, resulting in a shift of the reconstructed SST of 1 to 2 degrees Celsius.

2.1.2 Long-term carbon cycle

A distinction is made between the short-term and the long-term carbon cycle. The short-term cycle includes brief interactions between the ocean, the atmosphere, biosphere and pedosphere, such as river transport, gas exchange, photosynthesis or respiration. This system stabilizes quickly around a timeframe of several hundred years and tends to reach a steady state. For a geological timescale, that being over millions of years, gradual long-scale dynamics could produce a constant shift by removing or adding carbon from the influence of the short cycle. Carbon can be buried and trapped as organic matter or carbonate in sediments. Volcanic or metamorphic outgassing as well as weathering can recycle the stored carbon (Fig. 1).

2.1.3 Astrochronology

The gravitational interaction between the planetary bodies in the solar system effects Earth's orbit in a periodic manner. The first calculation of this orbital parameters was conducted by Milankovitch (1920) who identified three distinct cycles (the now called Milankovitch cycles). These variations influence the total insolation and its distribution around the globe.
The eccentricity cycle describes a deviation of the Earth's orbit from a perfect circle, obliquity is a measure for the tilt of the Earth's axis and precession is the concept of the wobble of the Earth's axis and the rotation of the orbital ellipse. Variation in the insolation leaves a mark in the sediment record. Spectral analysis is used to filter any record for the imprint of the Milancovitch cycles (and therefore climatic change). We use fourier transformation to recognise individual frequencies and periodicity and identify particular Milancovitch cycles.
The assignment of the periodicity in any time series to orbital parameters allows us to develop an absolute cyclostratigraphic age model (if anchored to today)
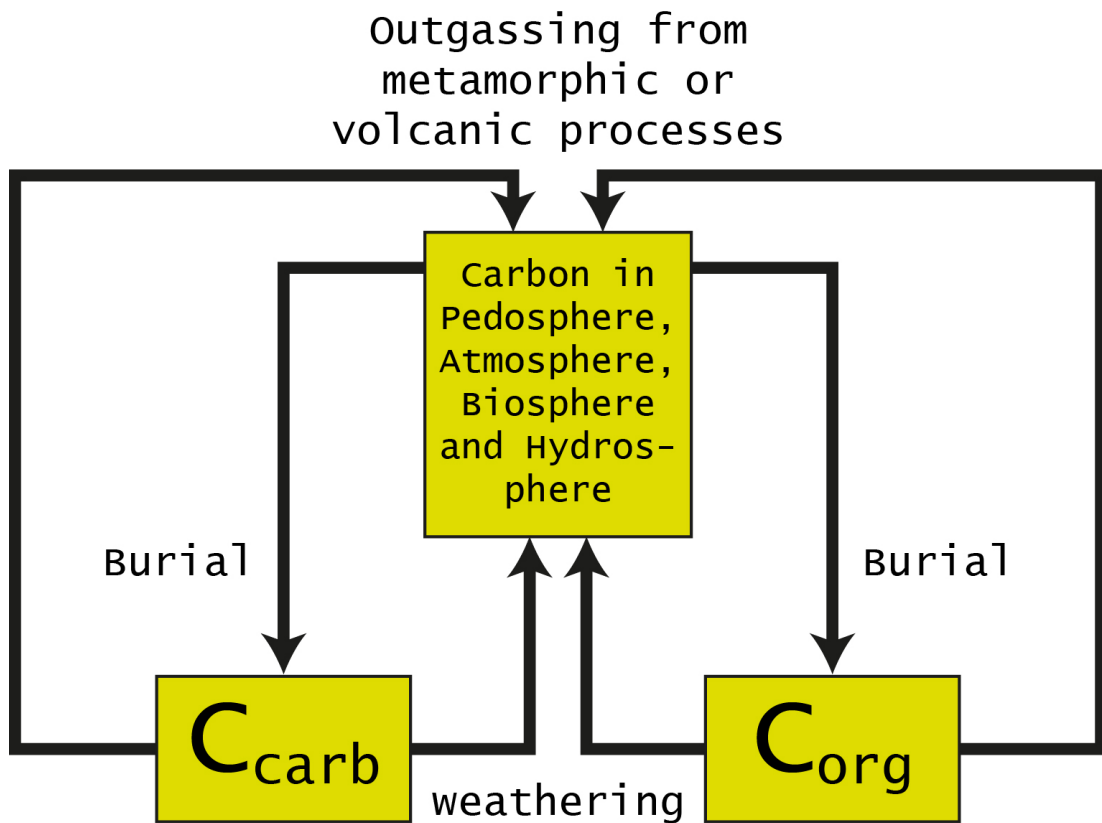
Figure 1: The long-term carbon cycle

because we know the length of the Milankovitch cycles and can "simply" count the amounts of cycles in the record.

This method works with a high confidence and is indeed used to establish a highly detailed time scale for the whole Cenozoic. Further approaches reach back to the Mesozoic or even Paleozoic.

2.1.4 Case studies

An important time of climate warming during the Cenozoic was the PETM, the Paleocene-Eocene Thermal Maximum at the Paleocene/Eocene-boundary around 55 Ma ago with a duration of over 100,000 years. It is defined by a global warming of around $4 - 5\,°\mathrm{C}$ (with spatial variability) as proven by TEX_{86}-values and a negative δ^{18}O-excursion in benthic foraminifera carbonate that due to the lack of ice in the Paleogene can be attributed to ocean warming. An increase in river runoff and sediment supply is evident just as a deoxygenation in the oceans. Several continental margins even became anoxic during the PETM.

The warming can be explained by a massive carbon input into the system, as shown by a negative δ^{13}C-excursion, and the enhanced dissolution of carbonate in ocean sediments, an evidence for an advancing acidification of the ocean. There are several hypotheses for carbon sources for the PETM. Possible causes are for example the thawing of methane hydrates (Dickens et al., 1995), the rapid release of carbon stored in permafrost soils (DeConto et al., 2012), orbital

pacing or a combination of them.

2.2 Field work

One Sunday during the Summer school was spent on a field work practical at the famous Cretacous-Tertiary-boundary outside of Gubbio (Fig. 2). The boundary is visible as a clayey, dark sediment layer enriched in iridium. This place was one of the outcrops, where the hypothesis of a meteorite hitting the earth was concluded first due to the fact that iridium is a rare element in Earth's crust and mostly abundant in extraterrestrial bodies. The Paleogene limestone sequence, intercalated with thin marl layers, was analyzed in terms of thicknesses of the individual layers.

Figure 2: The Cretaceous-Paleogene-boundary near Gubbio, Italy at the 13th July of 2014. (own picture)

2.3 Practicals

The variation of thickness measured during the field trip was scanned with a frequence analysis to identify particular Milankovitch cycles within the record. We were using the statistics program **R** together with the package *astrochron* under GPL-3 licence. Astrochron provides signal processing like spectral analysis or time-frequency analysis. We explored different analysis methods like the Multitaper Method, how to demean or detrend stratigraphic series or using linear interpolation.

3   Description of the main results obtained

For my PhD project I mostly work on a cyclostratigraphic age model for the Mid-Eocene. It was very useful to receive a sound standing introduction into the establishment of age models using orbital cycles because I have not been that familiar with Milankovitch cycles before.

The most important point for me was to learn about all the different proxies like stable isotopes, organic compunds and trace metals. All proxies are in a constant process of calibration, recalibration and interpretation and it is difficult to adjust ones measurements correctly with all the different influences from physical or ecological parameters which could produce a shift for the reconstructed paleo value, be it for example temperature or productivity.

4   Projected Publications / articles resulting or to result from the grant

The knowledge I acquired during the USSP provides a good basis for my research. At this point, it is too early to name any particular publication, but the ESF grant will of course be mentioned in the acknowledgements of future papers.

5   Other comments

Especially for graduate students who just started their work the USSP is a great opportunity to achieve a comprehensive introduction in the broad field of paleoclimate research. They can catch a glimpse of related scientific topics and approaches and learn about state-of-the-art scientific methods and brand-new results from leading paleoclimatologists. Additionally, it is a great chance to get in contact with fellow PhD students and senior scientists from all over the world which could led to interesting cooperations or sharing of knowledge.

I want to express my sincere thanks towards the European Science Foundation for giving me the possibility to participate in the Urbino summer school of Paleoclimatology.

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