

ESF Exploratory Workshop (co-sponsored by the Hanse Institute for Advanced Study)

“The Ocean Carbon Cycle and Climate Change”

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Scientific Report

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1. Executive summary

An interdisciplinary group of 34 scientists convened at the Hanse Institute for Advanced Study (HWK) in Delmenhorst (Germany) from September 1 through 4, 2001, in pursuit of the following goals: (1) to discuss scenarios of positive and negative feedbacks between the global carbon cycle and climate change on different timescales, (2) to better define proxies for recording oceanic carbonate chemistry dynamics and (3) to establish state-of-the-science and directions for the paleoceanography community to explore in the future. Besides these three main issues we (4) discussed research strategies and funding possibilities.

During the first day of the workshop 8 plenary talks set the stage for the subsequent working group sessions. In this session, the state of the science with respect to essential aspects of the ocean carbon cycle and climate change were presented:

- **Iron fertilization and export productivity.** Viktor Smetacek explained the present day functioning of the biological pump in the Southern Ocean, the impact of iron fertilisation via dust and ice bergs, changes in the species composition during blooms and how these could possibly affect export production today and during the glacial.
- **Decoupling of lysocline and saturation horizon: mission impossible?** Heiko Jansen introduced a box model that was developed to address the controversy between $\delta^{11}\text{B}$ based glacial ocean pH reconstructions and observed shifts in lysocline depths. He demonstrated that within reasonable glacial boundary conditions and without violating the sedimentary evidence, respiration induced pore water dissolution, can decouple the lysocline from the saturation horizon and explain up to 50 ppmv of the glacial pCO_2 shift but not the full shift as predicted by $\delta^{11}\text{B}$.
- **New insights on the incorporation of geochemical carbonate ion proxies into foraminifera.** Ann Russel demonstrated that G-IG variations in the U-record extracted from foraminiferal shells are too large to be explained by changes in the U-inventory alone. She presented results from laboratory culture experiments showing a negative correlation between U/Ca in the shells of planktonic foraminifera and the carbonate ion concentration of the culture water. This empirical relationship can explain the observed increase of U/Ca ratio in foraminiferal shells during the deglaciation to constant Holocene values by inferring a decrease in the carbonate ion concentration during the deglaciation to constant Holocene values.
- **Orbital- and millennial-scale variations in the global carbon cycle.** Yair Rosenthal stressed the fact that, due to changes in the solubility pump and the terrestrial carbon inventory, ca. 120 ppm difference in atmospheric carbon dioxide content on glacial interglacial timescales need to be explained. Different systems and mechanisms may be involved on different timescales.
- **The role of carbon dioxide in the ice age cycles.** Nick Shackleton showed that by combining benthic marine $\delta^{18}\text{O}$ records and the Vostok $\delta^{18}\text{O}$ air record, deep-water temperature variability, ice volume changes and the variability of the Dole effect can be separated. These deconvoluted signals show that changes in atmospheric CO_2 , Vostok air temperature as well as deep-water temperature are in phase with orbital eccentricity and lead ice volume changes, suggesting that a response of the global

carbon cycle to changes in orbital eccentricity could play a central role in generating the 100ky cycle in paleoclimatic records.

- **Tropical Temperature Leads on Glacial Terminations.** David Lea generated a record of ice-volume change by substituting Mg/Ca temperatures into a planktonic foraminiferal $\delta^{18}\text{O}$ record and solving for $\delta^{18}\text{O}_w$. The equatorial Pacific record shows that temperature leads ice volume by 3000yr. Because the tropical Pacific sea surface temperature change is in phase with the Antarctic air temperature this suggests that tropical cooling plays a major role in driving ice-age climate.
- **Carbon isotope linkage between the tropics and the Southern Ocean during glacial terminations.** Howard Spero presented multi species isotope data of planktonic foraminifera from the equatorial Pacific supporting the view that glacial interglacial differences in atmospheric $p\text{CO}_2$ may be explained by a mechanism in which Antarctic sea ice prevents out-gassing of CO_2 during the glacial.
- **Some modelling aspects.** Ernst Maier-Reimer discussed global biogeochemical cycle models, including GCM's and box models. The main emphasis was on the distribution of carbon, alkalinity and nutrients as simulated by the HAMOCC. Present day models change the Holocene oceanic carbon cycle in order to reach glacial values. However, since the Earth is most of the time in a glacial state interrupted by warm phases, it is necessary to follow the opposite approach.

A visit to the new Science Center "Universum" in Bremen and a conference dinner closed the first day. The morning session of the second day was used to present two EC projects dealing with pertinent aspects of the global carbon cycle and climate change and to learn about ESF funding options. Howard Spero presented a summary of the first day plenary session and highlighted the challenges for the upcoming working group sessions. The discussion leaders (DL's) introduced topics for discussion in 4 possible working groups. Consensus was reached to establish 3 working groups that convened separately for the rest of the day:

- **Biological pump and nutrient dynamics** (DL: Smetacek; R (rapporteur): Peeters/Brummer). The Southern Ocean has always been pointed at as an important sink for glacial CO_2 . Based on sedimentary evidence and the present day structure and operation of the biological pump can we assess its role in the glacial?
- **Reconstructing and modeling past ocean carbonate chemistry** (DL: Erez; R: Hönisch). Assessment of G-IG changes in the carbonate chemistry is the basis for understanding the role of the ocean carbon cycle in the climate system. Which proxies are available and how robust are they? What do we already know about the dynamics of the carbonate system over G-IG time scales?
- **SST, ice-volume and CO_2 : linkages, leads and lags** (DL: Lea; R: Bijma). Leads and lags between proxy parameters are crucial for a mechanistic understanding of the climate system. What is the state of the art, what are the pitfalls and where should we go from here?

In the evening, Jonathan Erez presented his research on the calcification mechanism in benthic foraminifera. An impressive video documented his experimental work (using fluorescent dyes in confocal microscopy) on *Amphistegina lobifera*.

During the morning session of the third day the working groups reconvened. After lunch, the working group output was presented by the discussion leaders (see working group reports under 2. Scientific content) and discussed in a plenary session. The recommendations of the working groups are presented below:

WG1: Biological pump and nutrient dynamics

- A better mechanistic understanding of the biological pump may be acquired from modern ecosystem shifts such as occurring in the Bering Sea, California Current and in lake-environments. Seasonal changes may also be considered as short-term ecosystem shifts and should be studied in this perspective. Both the functional groups and the trophic structure of the biological pump need to be understood.
- The role of macro- and micro-nutrients in different environmental settings needs further clarification. Particular aspects of the N-cycle (lightning, denitrification, N₂-fixation, dust deposition) and micro-nutrients (Fe) are poorly understood, as are changes in the Redfield ratios. Consider scenarios such as "Fe-limitation leads to inefficient nitrate/phosphate utilisation but not silica".
- It appears that most processes relevant to the biological pump are located on continental margins and in seasonally high-productivity areas. However, it has been suggested that N₂ fixation in the subtropical gyres is limited by Fe availability and that these regions could bind a significant amount of carbon if they were P- rather than N-limited. A multidisciplinary approach should include integrated studies on biological production, settling flux and burial processes. Proxies for differential nutrient limitation need to be developed to corroborate paleoceanographic inferences on G/IG timescales (e.g. frustule thickness of diatoms for Fe-limitation?).

WG2: Reconstructing and modeling past ocean carbonate chemistry

- Ideal proxy-relationships do not exist the influence of many of the interfering parameters can be corrected for, if the nature of the interferences were known and other proxies are applied to estimate the magnitude of the specific error.
- To increase the robustness of proxy-relationships detect possible interferences, a multi-proxy approach should be followed.
- Laboratory culture experiments, field verification and process modeling should go hand in hand.
- A better understanding of the biomineralization mechanisms of the major groups that provide proxies is required. Only with such an understanding it will be possible to explain the deviations of proxy relationships from thermodynamic predictions (inorganic precipitation experiments).
- The effects of dissolution and other diagenetic changes need to be studied.

WG3: SST, ice-volume and CO₂: linkages, leads and lags

- Tie marine records to ice core stratigraphy using proxies with the highest climate signal to noise ratio (e.g. $\delta^{18}\text{O}$ of benthics to ice core air $\delta^{18}\text{O}$, North Atlantic surface water records to Greenland isotopic and CH₄¹ variations, and marine $\delta^{18}\text{O}$ water records to air $\delta^{18}\text{O}$ records).

¹ The advantage of methane is that it is present in both Greenland and Antarctic cores.

- Multiple proxies should be determined on each core and samples shared between laboratories (added value).
- Preparation and analysis protocols should be standardized (“cookbook”).
- Proxies determined on the same phase are particularly suited for tuning purposes.
- To understand cause and effect relationships on orbital timescales requires higher frequency variability (millennial, centennial) to be identified and locked in on a common time scale
- Focussing on events or time slices alone (e.g. glacial terminations, Younger Dryas) conceals information on processes leading into these events.
- Better a few high resolution cores than many low resolution cores².
- Cores below long time series stations are especially valuable.
- The absence of a cold MIS VI interval in alkenone unsaturation records requires be investigated.
- The observation that alkenone records are ca. 2-5kyr older than foraminifers from the same sample throughout a core requires further investigation
- mapping ash layers in the Pacific (XRF) is suggested for tying planktic and benthic records to ice-core records.

Acknowledgements

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² Please note that modelers prefer many lower resolution cores as they require horizontal coverage

2. Scientific content

By bringing together European and American experts in the fields of paleoceanography, chemistry, biology and physics, the workshop has contributed in highlighting some important issues that require our attention in order to force a breakthrough in our understanding of the interrelationships between the ocean carbon cycle and climate change:

- WG1:** The Southern Ocean has always been pointed at as an important sink for glacial CO₂. Based on sedimentary evidence and the present day structure and operation of the biological pump can we assess its role in the glacial?
- WG2:** Assessment of G-IG changes in the carbonate chemistry is the basis for understanding the role of the ocean carbon cycle in the climate system. Which proxies are available and how robust are they? What do we already know about the dynamics of the carbonate system over G-IG time scales?
- WG3:** Leads and lags between proxy parameters are crucial for a mechanistic understanding of the climate system. What is the state of the art, what are the pitfalls and where should we go from here?

These were the challenges for the three working groups. The outcome is detailed in the following working group reports which form the basis for publications to be submitted to G³.

WG1 report: Biological pump and nutrient dynamics

Participants: Wolfgang Berger, Geert-Jan Brummer (R), Jean-Pierre Gattuso, Anders Lindroth, Svetlana Patsayeva, Ernst Maier-Reimer, Frank Peeters (R), Ulf Riebesell, Victor Smetacek (DL), Stefan Schouten, Sonja Schulte, Klaus Wallmann, Patrizia Ziveri.

1. Introduction

Working Group 2 “Biological pump and nutrient dynamics”, consisted of scientists from various countries and disciplines. In this report we discuss the role of the biological pump at present and in the near future, while drawing on evidence from the past. Below, we give a brief overview of the main points discussed during this session. Each paragraph below will start with a question that relates to a certain aspect of the biological pump. Hereafter, the most important comments and remarks discussed in the working group are given.

2. What do we know of today’s pump: magnitude and budgets

The biological pump is dependent on a wide range of interdependent factors and can be approached from various angles such as ocean circulation, nutrient dynamics and ratios, biological processes. In addition, space and time scales and their variability have to be considered. The following numbers were used to discuss different aspects of the biological pump. The total oceanic carbon budget is estimated at 34 000 Gt. C. The annual net primary production (NPP) amounts to 40-50 Gt C yr⁻¹ of which about 10 Gt C±50% is exported from the productive surface layer to the ocean interior. Only 0.2 Gt C±50% is buried in the geological reservoir. Since a number of processes drive the biological pump (sinking aggregates including algal cells, zooplankton feces, vertically migrating zooplankton, subduction and deep mixing of surface water with its suspended POC and DOC loads etc.)

inter-annual variation can be significant. Also the origin and composition of organic matter is poorly characterised: to what extent is the ocean's DOC composed of refractory terrestrial compounds; how selective is the preservation of specific organic compounds; what are the biological producers and modifiers (bacteria, organic-walled dinoflagellates, spores)?

3. What are the sinks and sources of nutrients and the role of biological production in the nutrient cycle?

Biological productivity in the ocean, and the transfer of fixed carbon from the surface ocean to the deep sea, is ultimately limited by the availability of nutrients and is predominantly governed by P, N, Fe and Si. Scenarios based on the numbers mentioned above are less robust than it appears. For example "new" P is released from continental margin sediments after reduction of the iron-minerals to which the P is bound. Significant quantities of N-nutrients may be produced by lightning or introduced by biological N₂ fixation in N-limited areas, e.g. in the central gyres. On the other hand, denitrification removes nitrate in suboxic layers or sediments. Both the relative and the absolute contribution of these processes are poorly constrained. Furthermore, micro-nutrients such as Fe, apparently govern the poor efficiency of the biological pump in the HNLC areas (High Nutrients Low Chlorophyll) such as the Southern Ocean and oceanic upwelling zones (Equatorial and Subarctic Pacific). In addition to iron, all other nutrients may also be introduced by atmospheric dust. Variations in dust input, which are known to have occurred on glacial/interglacial (G/I) time scales, may therefore have important consequences for the biological pump.

On a global scale, the distribution of nutrients is governed by ocean circulation and biological productivity. Therefore, nutrient concentrations and Redfield ratios differ between ocean basins. For example, biological productivity in the HNLC areas is limited by the availability of Fe, whereas productivity in the subtropical gyres appears to be limited by the availability of N-nutrients. Physical processes may remove unused nutrients from the photic zone by downwelling, whereas upwelling of macro-nutrients contributes little to the (export) productivity since micro-nutrients (Fe) are not supplied concurrently.

Since the trophic structure changes according to the limiting nutrients, the composition and magnitude of the (export)production of organic matter will change in concert. Structural changes in the biological pump will occur in response to the environment/climate and include:

- The functional groups that constitute the productive biomass. For example, Si limitation will suppress diatom production but not that of *e.g.* Phaeocystis and coccolithophorids.
- The species-specific response within the functional groups, such as the change in the N:P ratio as a function of the Fe concentration in diatoms.

With respect to the question whether Redfield ratios are constant over geological time, there is now evidence that these ratios shift depending on the specific nutrients that are limiting the ecosystems and their constituent populations.

4. What can be expected of the biological pump in the context of global change?

With respect to the importance of the biological pump to climate change, it is the change in the intensity and magnitude of the pump that matters. Such changes not only occur on time scales of thousands of years, but are currently ongoing for example in the Bering Sea and the California Current. In the Bering Sea, massive coccolithophorid blooms have occurred since 1997, in an area where the phytoplankton communities are usually dominated by diatoms, siliceous phytoplankton. These blooms are visible on SeaWiFS true colour satellite images as

turquoise, bright waters, caused by the reflection of light by the calcareous coccoliths (http://daac.gsfc.nasa.gov/CAMPAIGN_DOCS/OCDST/bering_sea.html). Although the causes for this phenomenon are still not understood, they may result from changing circulation patterns in the Pacific Ocean. These regime shifts have a major impact on the entire food chain of the area, leading for example to a decrease in salmon stocks and massive bird starvation (Hunt, 1999; Stockwell et al., 2001; Napp et al., 2001). This illustrates the need for a better understanding of the causes and consequences of ecosystem change and the associated feedback mechanisms, since their effects in the Bering Sea will differ from those in the California Current. The geological record provides numerous examples of a single species or group dominating entire assemblages, and therefore may be interpreted as the remains of large past blooms.

In the near future, ecosystem changes are expected to result from modern global warming. Two consequences for the biological pump are likely to occur as a result of a reduced thermohaline circulation. First, the biological pump will be more efficient since nutrients are longer exposed in the photic zone. Second, nutrients will be trapped longer in the deeper ocean while surface waters become more depleted. However, other mechanisms will regionally modify the efficiency and capacity of the biological pump: the ventilation with intermediate water and the seasonal climatological conditions (e.g. monsoonal upwelling). Particularly the interaction between intermediate waters and continental margins is important considering the significant quantities of sedimentary organic matter (including methane hydrates) and Fe-bound P that may be remobilised. The impact of hydrographic changes on the biological pump on G/I time scales is considerable and may have affected both its efficiency and capacity. There is evidence, for example, that the thermocline during the Last Glacial surface ocean was relatively enriched in P and Fe but depleted in Si.

5. Research needs and recommendations

In general, the research needs and recommendations given below focus on specific areas and on specific processes that are important to the biological pump:

- A better mechanistic understanding of the biological pump may be acquired from modern ecosystem shifts such as occurring in the Bering Sea, California Current and in lake-environments. Seasonal changes may also be considered as short-term ecosystem shifts and should be studied in this perspective. Both the functional groups and the trophic structure of the biological pump need to be understood.
- The role of macro- and micro-nutrients in different environmental settings needs further clarification. Particular aspects of the N-cycle (lightning, denitrification, N₂-fixation, dust deposition) and micro-nutrients (Fe) are poorly understood, as are changes in the Redfield ratios. Consider scenarios such as "Fe-limitation leads to inefficient nitrate/phosphate utilisation but not silica".
- It appears that most processes relevant to the biological pump are located on continental margins and in seasonally high-productivity areas. However, it has been suggested that N₂ fixation in the subtropical gyres is limited by Fe availability and that these regions could bind a significant amount of carbon if they were P- rather than N-limited. A multidisciplinary approach should include integrated studies on biological production, settling flux and burial processes. Proxies for differential nutrient limitation need to be developed to corroborate paleoceanographic inferences on G/IG timescales (e.g. frustule thickness of diatoms for Fe-limitation?).

WG2 report: Reconstructing and modeling past ocean carbonate chemistry.

Participants: Wolfgang Berger, Christina Crone, Jonathan Erez (DL), Bärbel Hönlisch (R), Heiko Jansen, George P. Lohmann, Guy Munhoven, Martin R. Palmer, Ann D. Russell, Howard J. Spero, Dieter A. Wolf-Gladrow, Richard E. Zeebe, Patrizia Ziveri,

1. Introduction

On glacial-interglacial time scales oceanic carbonate chemistry determines atmospheric $p\text{CO}_2$. However, the underlying mechanisms and possible feedbacks with climate change are still not well understood. Knowledge of the nature and amplitude of natural fluctuations in the past can be used to assess the stability of modern subsystems and their potential range of variations in the future. Understanding the climate system therefore requires the reconstruction of physical, chemical and biological parameters that characterize the ocean carbonate system over glacial and interglacial time scales as well as the transitions between them. Over the past decade a number of proxy relationships based predominantly on foraminifera has been established on the basis of laboratory and field experiments. Among others, the stable boron isotopic composition in foraminiferal shells was found to record marine $p\text{H}$ (Spivack, 1993), Ba/Ca was used to infer alkalinity (Lea and Boyle, 1989) and differences between the influence of $[\text{CO}_3^{2-}]$ on the stable oxygen and carbon isotopic composition of *Globigerinoides sacculifer* and *G. ruber* was found to be useful for past carbonate ion concentration estimates (Spero, 1999; Bijma et al., 1999).

In addition to these proxies of the seawater carbonate system, the preservation state of carbonates can be used to estimate bottom water undersaturation for aragonite and calcite, by examining the depth of their lysoclines, which can be defined as the levels of maximum solution rate increase in the deep sea (Berger, 1968). Relating the preservation state of carbonates in the sediment to the saturation state of bottom water yields information on $[\text{CO}_3^{2-}]_{in\ situ}$. For example, the dissolution-driven shell-thinning of planktonic foraminifera was found to give a good approximation of bottom water $[\text{CO}_3^{2-}]$ (Broecker and Clark, 2001; Lohmann et al., 1999). More recently, some new proxies such as foraminiferal U/Ca (Russell, 2001; Russell et al., 2001), S/Ca (Erez et al., 2001) and the CaCO_3 size fraction index (Broecker and Clark, 1999) have been found to record $[\text{CO}_3^{2-}]$.

Unfortunately, the interpretation of these proxies is often biased by their dependency on additional variables. Species specificity, vital effects of the organisms, and even the susceptibility to diagenesis complicate data interpretation. Hence, proxy relationships are not as simple as we would like them to be. For example, the interpretation of geochemical proxies in surface-dwelling planktonic foraminifera is complicated by the presence of a significant fraction of calcite added at depth. Thus, since most calibrations are empirical, a certain discrepancy exists between laboratory experiments and the real situation on the seafloor. Combination of these proxy development approaches with better understanding of the calcification mechanisms and numerical models should yield higher reliability of these proxies. Eventually, such new data and its proper modeling would render further insight into the role and the impact of the carbon cycle on climate oscillations and in particular resolve the mechanisms that control the operation of the oceanic carbon cycle.

Working group 3 discussed the carbonate system proxies (Table 1) and their limitations. In order to obtain high-quality paleoreconstructions, future research needs to focus on the

removal of these uncertainties. Recommendations point towards field investigations and culture experiments, as well as towards numerical models and the improvement and further development of existing and new analytical techniques.

2. Proxies for ocean carbonate chemistry and their limitations

2.1 Carbonate chemistry

2.1.1 Ba/Ca to infer alkalinity

Ba is a nutrient-like tracer similar to Cd and $\delta^{13}\text{C}$, because biological activity extracts these elements from surface waters and gravitation transfers them toward the seafloor in sinking particles. On its way from the North Atlantic to the deep North Pacific, deep water is progressively enriched in Ba. The close correlation between Ba and alkalinity in seawater (Chan et al., 1977; Lea and Boyle, 1989) is mechanistically not well understood (Bishop, 1988; Chan et al., 1977; Chow and Goldberg, 1960; Klump et al., 2001; Lea, 1993; McManus et al., 1999), but is thought to be related to the simultaneous release of alkalinity through CaCO_3 dissolution and regeneration of Ba at the seafloor. However, Lea (1993) suggested that changes in the thermohaline circulation redistributes Ba and alkalinity similarly, thereby allowing reconstruction of past alkalinity distributions from benthic foraminiferal Ba/Ca.

The main limitation of Ba as a paleoproxy has recently been discussed (Hönisch et al., subm.). Briefly, due to the short oceanic residence time on the order of 10,000 years (Chan et al., 1976; Broecker and Peng, 1982), the Ba-alkalinity correlation is not perfectly applicable on a time scale longer than this period. However, the fact that Ba is incorporated into foraminifera shells in direct proportion to the seawater concentration (Lea and Boyle, 1989; Lea and Spero, 1992, 1994; Hönisch et al., subm.) allows us to estimate paleo-Ba concentrations from foraminifera deposited in sediments. Independent estimations of seawater carbonate chemistry would offer an opportunity to verify whether the present-day slope of the Ba-alkalinity relationship is applicable to the past as well. A multiproxy approach would provide the best means of calculating alkalinity for various time scales which can then be compared with the Ba concentrations recorded in foraminiferal shells.

2.1.2 $\delta^{11}\text{B}$ to infer $p\text{H}$

Inferring seawater $p\text{H}$ from stable boron isotopic compositions is based on the isotopic fractionation between dissolved boron in seawater and boron in CaCO_3 . The uncharged boron species $\text{B}(\text{OH})_3$ is enriched in ^{11}B by $\sim 20\text{‰}$ over the charged species $\text{B}(\text{OH})_4^-$. Of these two dominant aqueous species, it is the charged borate that is incorporated into carbonate minerals. As the fraction of $\text{B}(\text{OH})_4^-$ and $\text{B}(\text{OH})_3$ changes with $p\text{H}$, so must their respective isotopic compositions. The isotopic composition of boron in the CaCO_3 therefore is enriched with the heavier isotope ^{11}B with increasing $p\text{H}$ (Sanyal et al., 2000; Hemming et al., 1995).

The boron isotopic composition in carbonates is also highly sensitive to local variations in $p\text{H}$. The calcification process itself and microenvironments (like associations with symbionts or precipitation within extrapallial fluids) must therefore be considered. While the planktonic foraminifer *G. sacculifer* and benthic foraminifera appear to incorporate $\delta^{11}\text{B}$ with little or no fractionation compared to the theoretical curve, *O. universa* shows an offset from those foraminifera by $\sim 3.3\text{‰}$ (Sanyal et al., 1996). The offset was suggested to be due to a vital effect, although its nature could not be explained: both planktonic species are spinose and symbiont-bearing and should therefore react similarly.

The effect of symbiont photosynthesis has recently been investigated in a diffusion-reaction model by (Zeebe et al., 2001). They calculated a constant but significant offset between $\delta^{11}\text{B}$ in planktonic foraminiferal calcite and the isotopic signature of $\text{B}(\text{OH})_4^-$ in the bulk medium. A set of laboratory culture samples is currently being analyzed in order to test the model results.

Stable boron isotopic analyses, using negative thermal ionisation mass spectrometry (nTIMS), have several complications. First of all, the technique requires several hours of permanent operator assistance and numerous replicate analyses until accurate values can be obtained. Second, to achieve a reproducible result, approximately 4 ng boron are required per analysis. Since foraminifera contain 5-15 ppm B (Hemming et al., 1998), approximately 10 mg foraminiferal calcite are needed per sample (when considering weight loss during cleaning and multiple replicate analyses). Especially for the investigation of deep water chemistry the second point is crucial, as the abundance of benthic foraminifera is too low to routinely allow single-species analyses. Sanyal et al. (1995) therefore combined several species for their deepwater record in spite of possible differences in habitat (epifaunal/infaunal) characterized by a range of pH conditions, and species-specific offsets like the ones found for planktonic foraminifera (Sanyal et al., 2001). These factors (Sanyal et al., 1997, 1996) may have biased the obtained value, which suggested a 0.3 pH units increase for last glacial deepwater (Sanyal et al., 1995).

In order to solve the problems named above, it is desirable to reduce the amount of material required for analyses, to speed up measurements and to generally expedite the analytical procedure so that the investigation of past ocean acidity can be realised extensively in future work.

2.1.2 Deconvolution of the carbonate ion effect to infer $[\text{CO}_3^{2-}]$

This approach is based on the deconvolution of foraminiferal $\delta^{13}\text{C}$ records to calculate the change in surface $[\text{CO}_3^{2-}]$ and $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ through time: The stable carbon and oxygen isotopic compositions of planktonic foraminifera decrease with increasing carbonate ion concentration (Bijma et al., 1999; Spero et al., 1999). Among the investigated planktonic foraminifera, *G. sacculifer* and *G. ruber* share the same habitat but the slope in $\delta^{13}\text{C}$ vs. $[\text{CO}_3^{2-}]$ is twice as large in *G. ruber* as in *G. sacculifer*. This species-specific difference is used to distinguish between the effect of $[\text{CO}_3^{2-}]$ and a simultaneous change in $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$. Application to the sediment record leads to the estimate of $+55 \pm 63 \mu\text{mol kg}^{-1} [\text{CO}_3^{2-}]$ for the Indian Ocean during the last glacial (Spero et al., 1999). Unfortunately, this method is restricted to tropical surface waters, where *G. sacculifer* and *G. ruber* occur.

2.1.3 U/Ca to infer $[\text{CO}_3^{2-}]$

Laboratory experiments revealed that U/Ca in planktonic foraminifera shells is inversely related to $[\text{CO}_3^{2-}]$ (Russell, 2001). The symbiont-barren *G. bulloides* incorporates approximately twice U/Ca than the symbiont-bearing *O. universa* at the same $[\text{CO}_3^{2-}]$ (Russell et al., 2001). No consistent temperature effect on the record has been found above 19°C. Application of the U/Ca relationship to Caribbean cores suggested that glacial $[\text{CO}_3^{2-}]$ was $80\text{-}100 \pm 60 \mu\text{mol kg}^{-1}$ higher than during the Holocene.

Although the approach is generally promising, the study of several sediment cores revealed that contamination by Mn carbonates places a significant diagenetic overprint on the

incorporated U/Ca which may limit the general applicability of this proxy to sediments above the redox front.

2.1.3 $\text{SO}_4^{2-}/\text{CO}_3^{2-}$ to infer $[\text{CO}_3^{2-}]$

In laboratory culture experiments, (Erez et al., 2001) observed a constant distribution coefficient between $\text{SO}_4^{2-}/\text{CO}_3^{2-}$ in the shells of benthic and planktonic foraminifera and $\text{SO}_4^{2-}/\text{CO}_3^{2-}$ ratio in seawater. Since the seawater SO_4^{2-} inventory is not expected to have changed on glacial-interglacial time scales, $[\text{CO}_3^{2-}]$ can be reconstructed. *In situ* calibrations of this proxy in the Gulf of Eilat gave similar results to those of the laboratory experiments. However, in the Little Bahama Bank a temperature effect was revealed which may have been caused by changes in the Mg ion content, apparently affecting the SO_4^{2-} content of foraminiferal shells. Correction of this temperature effect leads to the empirical negative correlation between seawater $[\text{CO}_3^{2-}]$ and foraminiferal $\text{SO}_4^{2-}/\text{CO}_3^{2-}$ as found in laboratory culture experiments. Preliminary comparisons of $\text{SO}_4^{2-}/\text{CO}_3^{2-}$ from Holocene and glacial benthic foraminifera show variability in *pH* similar in magnitude to that estimated independently from $\delta^{11}\text{B}$ (approximately 0.2 *pH* units increase in the glacial deep Pacific).

The advantage of this proxy is that very small samples can be measured routinely using a Magnetic Sector ICP-MS. Hence it is practical to be used for benthic foraminifera from deep sea sediments. However, the proxy is still under development and not much is known about its limitations. One possible interference may be the contamination with extraneous phases like barite (BaSO_4).

2.2 Carbonate preservation

2.2.1 Size-normalized shell weight

The average mass of planktonic foraminifera is primarily determined by their size, but there is a measurable secondary relationship of shell mass to water depth (Lohmann, 1995; Lohmann et al., 1999; Rosenthal et al., 2000). Due to dissolution, the size-normalized mass of nearly all species is lower in deeper water than it is in shallow water, and the decrease is continuous over a wide range of carbonate saturation states, even well above the calcite lysocline. Based on shells of the three species *G. sacculifer*, *Pulleniatina obliquiloculata* and *Neogloboquadrina dutertrei*, (Broecker and Clark, 2001) determined an average weight-loss slope of $0.3 \pm 0.05 \mu\text{g} (\mu\text{mol kg}^{-1})^{-1}$ decrease in pressure-corrected deep sea carbonate ion concentration. This relationship allows estimates of changes in seawater carbonate content from the size-normalized mass of planktonic foraminifera.

To use the relationship as a paleocarbonate ion proxy, this method requires that the offset between pore and bottom water saturation is constant. However, numerous investigations (Archer et al., 1989; Berelson et al., 1990, 1994; Jahnke et al., 1994, 1997; Hales and Emerson, 1996, 1997) have applied microelectrodes and benthic flux chambers to validate the theory of respiration-driven dissolution *in-situ* (see also section 2.3.1). They conclude that 40-60 % of the calcite dissolution above the saturation horizon can be attributed to metabolic processes. The amount of organic matter reaching the seafloor varies between sites and depends on depth. Assuming increased productivity on glacial time scales, the magnitude of this effect might have been even stronger. Application of this proxy should therefore be restricted to locations where strong changes in paleoproductivity are not expected.

Another complication in the applicability of this proxy is the initial increase of the average shell weight of a freshly sedimented foraminiferal population: At the initial stages of

dissolution (probably still above the lysocline) the thin shelled, light weight individuals disintegrate first. Since thin shelled individuals are isotopically lighter, the increase in foraminiferal $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ can be attributed to the loss of these shells from the sedimentary community and thus confirms this finding (Erez, 1979a, 1979b). The maximum weight per individual is indeed shown by Lohman's data slightly above the lysocline. It should also be noted that the dissolution rate of foraminifera is not a linear process. This is due to the exponential increase of the specific surface area of a foraminifera with dissolution (Honjo and Erez, 1978) and to the non-linear nature of calcite-dissolution as a function of undersaturation (Keir, 1980).

An intriguing factor is also the dependency of the proxy on the target parameter itself, i.e. deep $[\text{CO}_3^{2-}]$ is not the only factor that determines the preservation state of foraminiferal shells within the sediment. The shell weight also depends on surface $[\text{CO}_3^{2-}]$ during precipitation of the shells. For instance, it can be demonstrated that for a glacial increase in surface water $[\text{CO}_3^{2-}]$ on the order of 55-100 $\mu\text{mol kg}^{-1}$ (as determined from U/Ca and carbonate ion effect), the shell weight of *G. sacculifer* increases by approximately 1.6–2.9 μg .

In addition, foraminifera shells from glacial conditions may be smaller than their interglacial counterparts. A detailed examination of available culture and sediment trap data is required to better estimate the magnitude of the observed growth effect and to determine how temperature affects the carbonate dependent growth variability at a certain locality over glacial/interglacial time scales.

2.2.2 Reflectance/ lightness of foraminiferal shells

A qualitative estimate of carbonate corrosion prior to foraminiferal test fragmentation is the combination of weight and light reflectance measurements of planktonic foraminiferal tests of the polar species *Neogloboquadrina pachyderma* (sin.). The method was developed by Helmke and Bauch (in press) and is restricted to regions and time intervals where carbonate preservation is generally good. Carbonate corrosion leads to changes in the surface structure of the calcite crystals and has a profound influence on the reflectivity of foraminiferal tests. An inverse relationship between light reflectance and weight was found. Application to Nordic Sea sediments revealed better preservation during glacial periods, which is consistent with higher deep sea $[\text{CO}_3^{2-}]$ for this time scale. However, the method is yet far from being used for quantitative estimates.

2.3 Estimating coccolithophorid paleoproductivity

Coccolithophorids are major contributors to the biogenic carbonate content in deep-sea sediments (Milliman, 1993; Westbroek et al., 1993; Archer et al., 2000). Recently, there has been increased interest in utilizing the elemental and isotopic chemistry of coccoliths. The chemistry of coccolith carbonate may record different information than that of foraminiferal carbonate because coccolithophorids, unlike foraminifera, are primary producers. Knowledge about their paleoproductivity is of major importance for e.g. rain ratio estimates and $\delta^{13}\text{C}_{\text{alkenone}}$ -based paleobarometer reconstructions (for review: Laws et al., 2001).

One limitation in the use of coccolith carbonate for geochemical studies has been the inability to “pick” monospecific coccolith assemblages for analysis, due to the very small sizes of coccoliths. New techniques now permit separation of fractions whose carbonate is highly dominated (>70 % and often >90 %) by a single coccolith species (Stoll and Ziveri, in press).

As with foraminifera, calcite produced by different species of coccolithophorids has different minor element partitioning and oxygen and carbon isotope fractionations.

2.3.1 Coccolith Sr/Ca and stable carbon and oxygen isotopes to infer growth rate and cell size

The Sr/Ca ratio of coccoliths was recently proposed as a potential indicator of past growth rates of coccolithophorids on the basis of correlations between Sr/Ca ratios in polyspecific coccolith samples and primary productivity, alkenone-estimated growth rates, and CaCO₃ rain rates in deep sediment traps (e.g. Stoll and Schrag, 2000) across the Equatorial Pacific upwelling region. Subsequently, a number of culture studies have investigated controls over Sr/Ca ratios in coccoliths of several species. For identical temperature and media composition, Sr partitioning is linearly related to rates of calcite production/cells (Stoll et al., 2001). Higher calcification per cell at higher growth rates observed in light-limited cultures of *Gephyrocapsa oceanica* and *Calcidiscus leptoporus*, as well as in *Emiliania huxleyi* cultures (Paasche, in press; Stoll et al., in press) may suggest that active uptake and calcification become increasingly important at higher growth rates. If coccolith Sr/Ca is a reliable indicator of coccolithophorids productivity, it would have the advantage of providing a record of past productivity variations directly from a primary producer. Furthermore, unlike many other mass-flux-derived productivity estimates, estimates from coccolith Sr/Ca would not rely on determination of sediment accumulation rates which are frequently imprecise.

Culture studies indicate different nonequilibrium effects in the oxygen and carbon isotope fractionations in different species of coccolithophorids (Ziveri et al., 2000, in prep.; Dudley et al., 1986). These nonequilibrium effects appear to reflect changing ecological and physiological responses of the organisms. In light- and nutrient-replete cultures, the nonequilibrium effects in $\delta^{18}\text{O}$ correlate highly with cell division rates across a range of species. At the same calcification temperature of 17°C and media composition, the $\delta^{18}\text{O}$ of the most common living species, *E. huxleyi* and *G. oceanica*, characterised by high cell division rates, are 3 ‰ offset with respect to equilibrium composition. In contrast, species with low growth rate such as *Umbilicosphaera sibogae* var. *foliosa* have a $\delta^{18}\text{O}$ fractionation effect of ~-2 ‰. Systematic relationships were also found between the carbon and oxygen isotopic composition of the coccolith calcite for each species and the surface area/volume ratio of the cells, which sets the diffusive flux of CO₂ available to the cell (Ziveri et al., in prep.).

Clearly, more work is needed to test the validity of this proxy in constraining coccolithophorid growth rates. Nevertheless, we are encouraged that qualitative or quantitative determination of past variations in species-specific algal growth rates may be possible with these tools.

2.4 Model results

2.4.1 Lysocline reconstruction

In a modeling study, Jansen et al. (subm.) evaluate the relationship between the lysocline and the saturation horizon. The results of Jansen et al. show that a combination of changing CaCO₃ and C_{org} production and an increase in the remineralization depth of organic carbon may have decoupled the lysocline and the saturation horizon during the LGM, suggesting that instead of the conservative estimate of 20 μatm , changes in the marine carbonate pump may have been responsible for a greater portion of the observed glacial/interglacial atmospheric pCO₂ shift on the order of 30-50 μatm .

Geological records suggest that during the last glacial, the Atlantic lysocline was 0.3-1 km shallower (Crowley, 1983; Curry and Lohmann, 1986), while it was about 0.8 km deeper in the Pacific Ocean (Farrell and Prell, 1989). Assuming that the lysocline has not changed its position relative to the saturation horizon, these changes correspond roughly to decreased atmospheric $p\text{CO}_2$ of 20 μatm (Broecker et al., 1991). However, the observed glacial/interglacial shift in atmospheric $p\text{CO}_2$ amounts to 80 μatm (Neftel et al., 1982; Petit et al., 1999). Additional reduction in atmospheric $p\text{CO}_2$ can be brought about by decoupling the lysocline from the saturation horizon, due to respiration-driven carbonate dissolution in the upper 10 cm of sediments, as observed e.g. by Hales and Emerson (1996). By changing the amount of organic carbon arriving at the seafloor, the amount of carbonate dissolution above the saturation horizon can change dramatically, shoaling the lysocline relative to the saturation horizon.

In contrast to the model used by Archer and Maier-Reimer (1994), Jansen et al. (subm.) do not consider the dissolution of CaCO_3 in the water column, as until now, the underlying mechanism of this proposed feature has not been found (Milliman et al., 1999; Jansen and Wolf-Gladrow, 2001; Jansen et al., subm.). Although this might result in an overestimation of the decoupling, it does not affect glacial/interglacial changes in the whole ocean carbonate inventory. Archer and Maier-Reimer (1994) tested scenarios for a glacial ocean where C_{org} production was three times as high and CaCO_3 production 60 % lower than at present. They concluded that such a variation, operated by a shift from calcareous to siliceous organisms during glacial times, might have driven atmospheric $p\text{CO}_2$ to glacial values. More recently, Sigman et al. (1998) argued that an increase in respiration-driven calcite dissolution has no significant effect on the decoupling of lysocline and saturation horizon as increased shallow water dissolution of carbonates would deepen the lysocline due to mass balance consideration. However, it is questionable whether carbonate production and dissolution are balanced at all (Milliman, 1993).

In contrast to Sigman et al. (1998), Jansen et al. (subm.) demonstrate that a decoupling of lysocline and saturation horizon is possible. However, respiration-driven dissolution can only significantly influence the atmospheric $p\text{CO}_2$ when the export ratio depends on primary production. Otherwise, the amount of organic carbon reaching deep-sea sediments would be too small. With fixed export ratios, variability in CaCO_3 production has a greater influence on atmospheric $p\text{CO}_2$ than variability in organic carbon production has.

Organic carbon productivity has been assumed to have increased during the LGM in the range of up to +100 % relative to today (Berger et al., 1989; Kumar et al., 1995; Paytan et al., 1996), while CaCO_3 productivity ranged between -60 % and +60 % relative to modern times (Kumar et al., 1995; Broecker and Henderson, 1998; Archer et al., 2000). These estimates yield $C_{\text{org}}:\text{CaCO}_3$ rain ratios that are comparable to modern rain ratios in high productivity areas. Thus, glacial $p\text{CO}_2$ levels of ~ 230-250 μatm $p\text{CO}_2$ are achieved within the assumed rain ratio ranges. The result of Archer and Maier-Reimer (1994), who found that the glacial to interglacial shift in atmospheric $p\text{CO}_2$ is completely explainable by a decoupling mechanism could not be reproduced by Jansen et al. (subm.). Rather, their model indicates that ~40-60 % of the glacial $p\text{CO}_2$ reduction may be attributed to changes in the marine carbonate pump.

3. Recommendations

The proxies and model results discussed above demonstrate that the ideal proxy-relationship does not exist. The record of a target parameter may be biased in several ways. However, the influence of many of the interfering parameters could be corrected for, if the nature of the

interferences were known and other proxies applied to estimate the magnitude of the specific error. To uncover possible interferences, further laboratory culture experiments on recorder organisms such as foraminifera and corals are required. The magnitude of these effects needs to be quantified through additional field data and process modeling. Not less important is a better understanding of the biomineralization mechanisms of the major groups that provide proxies (i.e. foraminifera, corals, coccolithophorids and diatoms). Only with such an understanding it will be possible to explain the deviations of proxy relationships from thermodynamic predictions and to verify whether such deviations are constant or require to be corrected for. Finally, the effects of dissolution and other diagenetic changes need to be studied in laboratory experiments and at depth.

3.1 Multi-proxy approach

The general advantage of preservational proxies (except examination with scanning electron microscopy) is their non-destructive character. The descriptive analysis of weight, light reflectance and general intactness leaves foraminiferal samples untouched and allows further chemical investigation. Apart from providing additional information on bottom water carbonate saturation, knowledge about the preservation state can furthermore help to elucidate possible interferences with dissolution effects on other chemical proxies like Mg/Ca. Adding chemical analyses to the interpretation of preservational proxies may reduce their own uncertainties. This could be for instance the application of U/Ca and $\text{SO}_4^{2-}/\text{CO}_3^{2-}$ to estimate surface water carbonate chemistry and its possible influence on weight and size of planktonic foraminifera.

Probably the most detailed knowledge on interferences exists in the field of chemical proxies in biogenic carbonates. Several culture studies on living foraminifera led to the establishment of empirical proxy-relationships and the discovery of some of their limitations (Bemis et al., 2000; Bijma et al., 1999; Erez and Luz, 1982; Erez et al., 2001; Lea et al., 1995, 1999; Lea and Spero, 1992, 1994; Mashiotta et al., 1997; Rink et al., 1998; Russell, 2001; Sanyal et al., 1996, 2001; Spero et al., 1997; Zeebe, 1999). Supplementary information to many of these proxies could be obtained by application of multi-element ICP-MS analysis on the same sample (Lea and Martin, 1996). However, for many parameters a reliable proxy does not even exist.

A crucial requirement to minimize uncertainties in the background information is therefore the search for new proxies for parameters such as salinity, productivity or deep sea carbonate chemistry. A first approach into this direction is given by the application of time-of-flight secondary ion mass spectrometry (TOF-SIMS, see section 3.3) to foraminiferal shell analysis. Furthermore, new recorders and proxies need to be found to reconstruct the conditions below the calcite compensation depth, where carbonates are already dissolved and no longer available

There is a clear need to combine available chemical and preservational proxies in order to improve the quality of paleoceanographic reconstructions. The importance of this so-called multi-proxy approach is not only valid for carbonate chemistry reconstructions, but for the investigation of leads and lags as well (see WG3 report).

3.2 Laboratory and field verification

As evident from previous sections, the establishment of empirical relationships in laboratory and field experiments and calcification studies are important steps towards the mechanistic

understanding of a proxy and its paleoceanographic robustness. Especially for the recently developed proxies it would be desirable to investigate these in more detail. Important aspects would be the U/Ca-calibration of the warm water species *G. sacculifer* and *G. ruber* and to obtain better information on the temperature dependency of the already existing relationships. The boron isotopic composition of planktonic foraminifera was recently suggested to be biased by temperature and partial dissolution (Wara et al., 2001). To question this finding, a set of planktonic foraminifera from a dissolution experiment is currently being analyzed. However, temperature effects will need to be investigated preferably in culture experiments, where other parameters can be kept constant. The effects of temperature and Mg on $\text{SO}_4^{2-}/\text{CO}_3^{2-}$ are currently being studied.

Although they are the most important recorders of deep water (carbonate) chemistry, benthic foraminifera are poorly represented in terms of experimentally calibrated proxy-relationships. Culture experiments are therefore required to expand our knowledge on already established and new proxies like U/Ca and $\text{SO}_4^{2-}/\text{CO}_3^{2-}$. It would be interesting to investigate if the carbonate ion effect on $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ is applicable to benthic foraminifera as well.

Culture experiments are an important tool but merely reveal a restricted picture of a proxy. Under natural conditions, planktonic foraminifera migrate vertically during their ontogeny and finally sink towards the seafloor, thereby experiencing variable water column conditions that modify their shell chemistry (e.g. Erez and Honjo, 1981; Lohmann, 1995). To further open this black box, plankton tow samples, sediment trap material, and surface sediment samples are needed to quantify the effects of this modification. Furthermore, dissolution experiments under simulated natural conditions are suggested to elucidate if part of the CaCO_3 is dissolved preferentially and thus, which proxies are affected by dissolution and to what extent.

With regard to possible contaminating phases, the $\text{SO}_4^{2-}/\text{CO}_3^{2-}$ proxy needs to be investigated in the light of special cleaning efforts. For foraminiferal Ba/Ca analyses, barite contamination was found to be removable by cleaning with an alkaline DTPA (diethylenetriamine-pentaacetic acid) treatment (Lea and Boyle, 1989). Cleaning experiments may help to determine the robustness of this $\text{SO}_4^{2-}/\text{CO}_3^{2-}$ proxy.

3.3 Recorders for deep water carbonate chemistry

As indicated in section 2.4.1, an increase of the marine carbonate pump under glacial conditions may have led to increased respiration-driven carbonate dissolution in the sediment. When arguing with sediment dissolution, the related diffusion of $[\text{CO}_3^{2-}]$ out of the sediment into the overlying bottom water needs to be considered to possibly having biased the glacial record, favouring locally more alkaline conditions than actually present in the deep water. At least for the Holocene this limitation can be tested. For instance the difference in $\delta^{11}\text{B}$ between *G. sacculifer* and benthic foraminifera appears to be similar in magnitude to the expected difference in pH between surface and deep water (Sanyal et al., 1995). However, how can we be sure that benthic foraminifera, that are living right at the sediment-water interface, always recorded deep water carbonate chemistry and not an anomalous local environment? To solve this problem, epibenthic deep water recorders are needed. For instance the chemical composition of the (less abundant) deep sea corals, ostracod shells or fish otoliths has hardly been investigated but these skeletal parts may possibly offer useful information with regard to deep and midwater (carbonate) chemistry.

3.4 Development of new methods

One possibility to reduce the amount of carbonate required for boron isotopic analyses may be the application of TOF-SIMS. This technique uses a focussed, energetic ion beam that detaches particles and ions from a sample surface. Furthermore, high resolution images can be obtained by scanning the surface of a sample with the beam of a liquid metal ion gun. The combination of surface imaging with depth profile capabilities allows the visualization of the three-dimensional distribution of elements in a foraminiferal shell. The overall advantage of this method is the simultaneous detection of all elements and masses on very small samples (single foraminiferal shells or less). The development of this method is still in progress. First results were published by Crone et al. (2000, 2001, *subm.*) and Vering et al. (2001). In addition to a substantial reduction of the amount of carbonate required for boron isotopic analyses, this analytical technique could simplify the establishment of new proxies. However, each analysis takes many hours to establish acceptable levels of precision, so that it is far from becoming a routine analytical tool.

3.5 Models

3.5.1 Thermodynamics of uranium uptake

In order to better understand the interaction between vital effects of a foraminifer and sea water chemistry, D.A. Wolf-Gladrow and A.D. Russell intend to develop a diffusion-reaction model comparable to Wolf-Gladrow and Riebesell (1997) and Zeebe et al. (1999).

3.5.2 Lysocline reconstruction

The existing box model of Jansen et al. (*subm.*) is a first approach to describe the processes that are important at certain sediment depth intervals. However, lysocline and saturation horizon shifted in opposite directions in the Atlantic relative to the Indopacific under glacial conditions (see section 2.4.1). In order to better estimate the global validity, the model is intended to be coupled to a global circulation model.

3.5.3 Boron isotopic fractionation in seawater

R.E. Zeebe is currently recalculating the stable boron isotope fractionation factor between $B(OH)_4^-$ and $B(OH)_3$. This value has never been measured and is fundamental to the boron isotope paleo-*pH* recorder.

WG3 Report: SST, ice-volume and CO₂: linkages, leads and lags

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1. Introduction

Leads and lags between climate events are a key to understanding how the Earth System operates. Cause and affect can only be determined with confidence if the resolution of the records is high enough and if the events observed in very different records (marine, terrestrial, atmospheric) can be locked into one common chronological framework. During the working

group discussions, we addressed several of these issues and focused on making recommendations for future work that would enable researchers to further elucidate leads and lags and their significance in paleoclimate records.

1.1 Time scales and timing

The primary step in determining leads or lags is to lock events or variables into a common chronological framework. There are three common ways to determine timing:

- Spectral analysis of records to determine phase angles: i.e., temperature vs. $\delta^{18}\text{O}$. This approach works best for long, orbital scale records.
- Relative timing (point by point): i.e., temperature vs. $\delta^{18}\text{O}_{\text{cc}}$, $\delta^{18}\text{O}_{\text{w}}$, $\delta^{18}\text{O}_{\text{O}_2}$
- Absolute timing:
 - Using ^{14}C dating. For events such as Termination I, this method works well if reservoir ages are known. However, at marine isotope stage (MIS) 3, for instance, the error in radiocarbon dating becomes already too much for determining leads or lags on the millennial scale with great confidence. The signal to noise ratio deteriorates and reservoir ages become more doubtful (e.g. Waelbroeck et al., 2001).
 - Using U/Th dating. This only works in areas with significant detrital aragonite such as tropical bank areas.

One of the major problems in determining leads and lags is to discriminate between, for example, the end of a millennial scale event and the beginning of the glacial Termination proper. Hence, the midpoint of a Termination is not a good operational tie point because it requires knowledge of the start and the end of the Termination. One solution to circumvent this problem would be to plot the envelope of the combined errors due to population variability, bioturbation and analysis on top of the point to point variability. Subsequently, periods of real change (point to point variability exceeds the width of the envelope) and stasis (point to point variability stays within the width of the envelope) may be more objectively distinguished. Another solution to determine leads and lags would be to tie points of most rapid change (i.e. where the second derivative of the primary function equals 0) because that does not require knowledge of the beginning and ending of the event.

Because ice cores with high accumulation rates, such as those from Greenland, can be dated very accurately (for instance, by counting annual layers with a precision of 3 years down to 1000 years; by ice dynamic modeling $\pm 1\text{-}3\%$ down to the LGM and $\pm \text{ca. } 5\%$ beyond 40ky BP), they provide the best absolute time scale. An example of locking marine records into an ice core timeframe is provided by Shackleton (2000), who utilizes the common spectral variability in the air and deep ocean oxygen isotope records. This introduces a new time scale for marine records that is synchronized to ice core time scales. An important question is how this time scale can be related to the venerable SPECMAP time scale, which is derived from orbital tuning of oxygen isotope records from low resolution marine sediment cores? The most obvious solution would be to tune benthics in any given core to Pacific reference core V19-30, on the south flank of the Carnegie Ridge (benthics are preferred as they do not contain the strong temperature signal present in planktonic foraminifera). Although the temperature contribution to the $\delta^{18}\text{O}$ signal in planktonics can be eliminated by using independent temperature proxies (Mg/Ca) this procedure would not take into account probable changes in the local precipitation-evaporation balance. If the latter are assumed to be insignificant, subsequent tuning of the planktonics could be done by tying the midpoints of fast events to the reference core by minimizing the residuals.

2. Proxy comparisons

Because each proxy has limitations, it is good practice to measure multiple-proxies on the same core. Proxies used for tuning purposes only require a high signal to noise ratio. The validity of the primary proxy relationship itself is less important. For instance, post mortem dissolution effectively lowers the recorded Mg/Ca temperatures in planktonic foraminifera (Rosenthal et al., 2000). Hence, surface temperature reconstructions at sites affected by dissolution result in temperatures that are too cold. However, even if the primary Mg/Ca temperature relationship is strongly affected by dissolution, a climate signal (in this case dissolution via changes in the saturation state of the bottom water) may still be clearly discernable.

This can be demonstrated when calculated core-top Mg/Ca temperatures of *Globigerinoides sacculifer* and *G. ruber* from the South Atlantic are plotted vs. Levitus temperatures (Drachenberg and Schneider, unpubl. Data). The Mg/Ca based reconstructed depth habitats for *G. sacculifer* and *G. ruber* plot between 50-75 m between 75-100m water depth, respectively. On the contrary, both species and especially *G. ruber* are known to inhabit the (upper) mixed layer and are therefore used routinely to reconstruct surface water properties. This discrepancy may be explained by assuming that the site is affected by dissolution, that *G. ruber* is more susceptible to dissolution than *G. sacculifer* and that dissolution drives Mg/Ca to colder temperatures.

In fact, it was suggested that dissolution indexes or proxies, e.g. “size normalized weight (Lohmann, 1995; Rosenthal et al., 2000) should be determined routinely on each core in order to assist in (re)interpreting the primary signal once the impact of dissolution on proxy relationships has been established (quality control). Paleoceanographers need to recognize the likelihood that many, if not all of the geochemical proxies recorded in foraminifer shells are affected by dissolution.

For proxy comparison, multiple proxies should be determined on the same core, and ideally that core should be located near a time series station where the local hydrography has been recorded over several decades (e.g. Bermuda Station S, Hawaiian Ocean Time Series). Alternatively, cores could be selected in key areas that are thought to be most sensitive to climate change, such as those where strong atmospheric gradients can be expected. Some areas may not be under the direct influence of such gradients but respond to climate change via teleconnections. Modelers can be helpful in finding such hotspots.

In order to compare and cross-check proxies, the geochemical information contained in foraminifer shells should be decomposed wherever possible into “clean” target parameters (i.e., temperature, ice-volume, etc.). However, in routine down-core analyses, it is equally important to have continued access to the raw data, in order to recalculate the target parameters once new information on the primary proxy relationships or the impact of diagenesis becomes available.

Proxies carried by different phases (e.g. U_{37}^k from coccolithophorids vs. $\delta^{18}O$ or Mg/Ca from planktic foraminifera) may be systematically offset in age for reasons such as differential bioturbation (Bard, 2001). For instance, it has been demonstrated throughout several cores that, the alkenone age was 2 to 5 kyr older than the foraminiferal age from the same level (Mollenhauer, unpublished data).

Another problem associated with proxies carried by different phases is that they may be telling different stories. For instance, the Mg/Ca record from a core near Galapagos showed normal G-IG cycles back to MIS 10 (data Lea, UCSB), whereas MIS VI was no colder than modern conditions in the alkenone unsaturation SST record from the same core (data Herbert, Brown). If such “anomalies” are not an exception but recur in different cores over the same time interval, as appears to be the case with the MIS VI alkenone unsaturation anomaly, the anomalies are probably telling us something important. Even if the Mg/Ca record fulfills the expectation, it does not necessarily mean that there is something wrong with the alkenone record. Apparently, additional information is contained in these “anomalies” and they may not be simply the result of differential mixing of two different phases. With regard to differential mixing one might argue that the coccolithophorids were simply absent during stage VI and that the stage VI signal must be produced by alkenones formed during the Eemian. Alternatively, one might argue that the species composition changed during stage VI, or that the discrepancy is indicative of strong seasonality during stage VI where the alkenones only recorded the warmest summers while the foraminifera document annual averaged temperatures. Yet another interpretation would invoke depth habitat shift of the foraminifers. Even though, the Mg/Ca record is anticipated and consistent with $\delta^{18}\text{O}$, it should be kept in mind that this can also be explained by a shift of the foraminiferal habitat below the thermocline. The reconstructed absolute temperatures may help to assess which scenario is most likely. If “inconsistencies” between proxies are noted, the first thing to do is to analyze a nearby core to see if they same inconsistency or anomaly is present.

There is not one proxy that is best suited for age tuning purposes. Although some proxies may be “better” than others in terms of precision, accuracy, resistance to diagenetic overprint etc., it should be kept in mind that local circumstances determine which proxy should be used. Some may be superior in some areas but worse in others. Some proxies may not even be present in certain areas. In general, it can be said that the best proxies for a certain setting are those with the biggest signal to noise ratio.

Recently, a lot of new insights on the limitations of primary proxy relationships came from groups growing foraminifera in the laboratory (Bemis et al., 1998; Bemis et al., 2000; Bijma et al., 1999; Spero et al., 1997; Spero et al., 1999; Wolf-Gladrow et al., 1999; Zeebe et al., 1999). This information should be incorporated into routine downcore analysis as well.

It was also noted that from a modelers point of view, it is important to estimate the quality (accuracy and precision) of proxies because small, unrealistic, features could otherwise incorrectly be used as climate forcing.

The fields of paleoceanography and paleoclimatology will always depend on proxies that are produced or affected by organisms, and even if some questions remain unsolved, the most important point is that we measure reproducible (consistent) variables and apply the same “microscope” to all cores. In order to produce a “cookbook” a conference on normalization and standardization should be envisioned similar to the one related to for instance normalizing SMOW to VSMOW.

3. Regional effects

It was argued that a few high quality, high resolution cores are preferable to several low resolution cores. On the other hand, for modeling purposes there is a need for good spatial coverage, and it is certainly not possible to obtain high resolution records in every area. Many high-resolution cores come from sites with a strong regional character and hence contain

(strong) regional hydrographic or temperature overprints. This is another reason why modelers are not necessarily keen on high-resolution cores. On the other hand, although regional effects also complicate the process of determining leads and lags, they may provide additional insight into how the climate system operates. For instance, contrary to most North Atlantic cores, downcore analysis of cores off Barbados and in the Angola Basin show warmer alkenone temperatures during the Younger Dryas or Heinrich event 1 (e.g. Rühlemann et al., 1999).

Critical samples should be replicated and a multiple proxy approach should be followed. If the differences recur, small scale modeling should be applied to validate both records in the sense that the differences can be explained in terms of regional variability in hydrography or temperature for instance.

Heterogeneity, especially in high resolution cores, should be viewed as an additional source of information telling us more than what was previously inferred from the one master site available in earlier days. Models can be used to identify hot spots that are key-players in the dynamics of the climate system. On the other hand, we should not forget that global modelers, at this stage, are more interested in a spatial coverage of many low resolution cores than in a regional high resolution data.

4. Global effects

Several processes create spatial and temporal heterogeneity complicating the deconvolution of leads and lags and hence of cause and effect. On the other hand, spatial and temporal heterogeneity provides crucial information for deciphering controls on climate change. Spatial heterogeneity may be hemispheric when remote sites are “teleconnected”, i.e., both records show similar signals (possibly differing in amplitude) but are phase shifted. Spatial heterogeneity may also be found when comparing open ocean and marginal settings because the latter may contain strong continental influences. On the other hand, if *Halimeda* is found in marginal settings it might provide a way of absolutely dating of millennial to orbital scale variability because it contains high concentrations of uranium.

Temporal heterogeneity refers to the differences found between the comparable marine isotope stages. For instance the heterogeneity between the Holocene, the Eemian and MIS11 or between Terminations I, II and V.

4.1 Spatial heterogeneity

Two modeling experiments were presented to demonstrate hemispheric heterogeneity via teleconnections: In the first example, Rodgers et al. (subm.) investigated the impact of a tropical temperature perturbation on the Laurentide icesheet. It is found that warming of tropical sea surface temperatures (SST) from glacial boundary conditions, as observed at the end of glacial periods (Bard et al., 1997; Lea et al., 2000; Nürnberg et al., 2000), causes a large increase in summer temperatures centered over the ice-sheet-forming regions of Canada. This high-latitude response to tropical change is due to alterations in the vertical profiles of temperature and moisture in the extratropical atmosphere. This atmospheric bridge represents a mechanism for deglaciation which is consistent with timing constraints (a phase shift of 3-5 ky). The strength of the response is mainly determined by the moisture increase from the warm Pacific (increasing back radiation), in combination with local topography. In contrast, a cold perturbation to tropical SST for interglacial boundary conditions results in almost no cooling over the Canadian region.

The second example offers a mechanistic explanation for the Southern Ocean lead over northern hemisphere deglaciation. Recently, it has been argued (Sigman and Boyle, 2000; Toggweiler et al., 1999) that changes in high-latitude Southern Hemisphere insolation trigger a Southern Ocean change, which then propagates to the high-latitude northern hemisphere, possibly through control of CO₂. Lohmann and Knorr (unpublished data) demonstrated a sequence of events in which warming of the Southern Ocean, followed by a retreat of the ice-margin, resulted in a decreased density of the ADW which enhances NADW formation. Enhanced NADW formation, in turn, increases heat transport from the Caribbean warm pool to the high latitudes. This mechanism (the oceanic seesaw) accounts for the main shortcomings of theories which rely on Northern Hemisphere forcing or internal ice sheet dynamics (Tarasov and Peltier, 1997) to explain deglaciation, namely the problem that the changes at high-latitude Southern Hemisphere occur before ice volume changes (Broecker and Henderson, 1998; Henderson and Slowey, 2000; Shackleton, 2000; Sowers and Bender, 1995).

4.2 Temporal heterogeneity

Terminations I, II, V show differences that may not be simply stochastic but the result of how the climate system operates. Similarly, the differences between the Holocene, the Eemian and for instance marine isotope stage (MIS) 11 may be indicative of the controls underlying climate change. Although much can be learned from such a direct comparison of events it should be kept in mind that time slices alone or a snapshot does not document the processes leading into the events. Hence, time series should be used for investigating temporal heterogeneity

5. Linking CO₂ to the carbon cycle

In order to determine leads and lags between atmospheric CO₂ and marine biological productivity, proxy records from marine sediments ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$, Mg/Ca, U_{37}^k ,...) need to be tied to records from the ice-cores (pCO₂, deuterium, CH₄, $\delta^{18}\text{O}_{\text{water}}$,...). With regard to $\delta^{13}\text{C}$, the best location for the marine record (highest signal to noise ratio) would be within the gyres where the ocean is in equilibrium with the atmosphere, allowing to correct for temperature dependent equilibration and hence to produce clean $\delta^{13}\text{C}_{\text{DIC}}$ signals. *Globigerinoides ruber* (distinguish between pink and white!) is suggested to be the most faithful recorder of surface water chemistry. Alternatively, the largest size fraction of *G. sacculifer* may be used (as they grew at the highest light intensities, i.e. at the surface). Except for choosing the right species, a large sample size (>30 specimens) is required to average out population variability.

Although $\delta^{13}\text{C}$ is clearly related to productivity, the signal is also affected by other processes (equilibration with the atmosphere; Suess effect and, locally, methane oxidation may affect $\delta^{13}\text{C}_{\text{DIC}}$). Dissolution proxies offer an alternative to tie pCO₂ to marine productivity. Several methods have been developed to date to measure dissolution: e.g. selective dissolution of foraminiferal species (e.g. Berger, 1970); composite index (e.g. Peterson and Prell, 1985a; Peterson and Prell, 1985b); "Lohmannology" (e.g. Lohmann, 1995; Rosenthal et al., 2000); CaCO₃ size distribution (Broecker and Clark, 1999); reflectance (e.g. Bauch et al., 2000). Dissolution related parameters ($\delta^{11}\text{B}$, U/Ca, S/Ca; see WG report on proxies) can also be used. These could be applied to cores that have been tuned to the ice-core record. Again, the proxy requirement is not so much a perfect calibration but a high signal to noise ratio.

Other productivity proxies that may be used include $\Delta\delta^{13}\text{C}_{\text{b-p}}$, benthic abundance (mass accumulation rates), benthic ratios (e.g. cibs in the denominator). Mass flux proxies should be corrected by thorium normalization. Yet another way to link marine productivity to atmospheric CO_2 (or temperature, ice volume, ...) would be to look for continental records in marine sequences (e.g. pollen, leaf waxes). Dust content offers another possible tie point and time of flight MS seems a promising development for generating rapid lithological records. It should be noted, however, that the dust signature in marine cores may have been transported a great distance before it was preserved in sediments and because it represents a different size fraction than foraminifera, it may be decoupled in time from $\delta^{18}\text{O}$ and Mg/Ca signals.

In high latitudes Heinrich events may offer a possible tie to ice-core temperature and CO_2 . The Heinrich chronology in the North Atlantic is converging and the magnetic events such as the Lachamps event offers an absolute time constraint. Similarly, ash-layer chronology offers lock-in points for tropical sediments and can possibly be tied to the Ar/Ar dated Ash Layer L or other such events.

Biological productivity proxies, in general, are susceptible to early diagenesis which has important consequences for tuning. For instance, as oxygen penetrates deeper into the sediments at the beginning of the deglaciations, the redox front deepens, shifting several proxy signals towards older horizons and hence effectively decoupling them from the $\delta^{18}\text{O}$ record.

Another example of decoupling involves the dust record in the Vostok ice-core: the lead of the dust suggested by Petit et al. (1999) disappears if plotted on a log scale. Although one could argue that the dust response to climate change is probably linear and not logarithmic, one might argue that a threshold (e.g. a minimum iron loading) needs to be reached before the biology kicks in.

6. Linking deep ocean to surface ocean

One of the big advantages of the deep ocean is that it is rather homogeneous and that therefore benthic records can be tuned based on absolute values! If nearby records don't give the same absolute value, the core should be resampled at higher resolution. This feature of the deep ocean also offers the possibility to produce absolute temperature gradients. However, because deep water temperature gradients are small, there is a strong need for inter-calibration (e.g. 0.5°C converts to 0.1‰): This requires, for example, that two standards (light and heavy) should be used for low latitudes sediments in which $\delta^{18}\text{O}$ of both planktics and benthics are being analyzed (Ostermann and Curry, 2000). In high latitudes, the $\delta^{18}\text{O}$ values of planktonics and benthics may be comparable but at low latitudes they can be up to 5‰ apart.

The infaunal habitat of several benthic species is probably not a severe problem with respect to tuning *per se* (as they will be mixed together with the planktics) but may complicate the amplitude of the records as pore waters can have a very different signal from bottom water.

7. Recommendations

- Tie marine records to ice core stratigraphy using proxies with the highest climate signal to noise ratio (e.g. $\delta^{18}\text{O}$ of benthics to ice core air $\delta^{18}\text{O}$, North Atlantic surface water records to Greenland isotopic and CH_4 ³ variations, and marine $\delta^{18}\text{O}$ water records to air $\delta^{18}\text{O}$ records).
- Multiple proxies should be determined on each core and samples shared between laboratories (added value).
- Preparation and analysis protocols should be standardized (“cookbook”).
- Proxies determined on the same phase are particularly suited for tuning purposes.
- To understand cause and effect relationships on orbital timescales requires higher frequency variability (millennial, centennial) to be identified and locked in on a common time scale
- Focussing on events or time slices alone (e.g. glacial terminations, Younger Dryas) conceals information on processes leading into these events.
- Better a few high resolution cores than many low resolution cores⁴.
- Cores below long time series stations are especially valuable.
- The absence of a cold MIS VI interval in alkenone unsaturation records requires be investigated.
- The observation that alkenone records are ca. 2-5kyr older than foraminifers from the same sample throughout a core requires further investigation
- mapping ash layers in the Pacific (XRF) is suggested for tying planktic and benthic records to ice-core records.

³ The advantage of methane is that it is present in both Greenland and Antarctic cores.

⁴ Please not that modelers prefer many lower resolution cores as they require horizontal coverage

3. Final Programme

September 1: Arrival of most participants and Icebreaker (19.00-22.00)

September 2 (plenary session):

- 9:00: **Jelle Bijma**: Introductory remarks; objectives of the workshop
9:20: **Viktor Smetacek**: Iron fertilization and export productivity
10:00: **Heiko Jansen**: Decoupling of lysocline and saturation horizon: mission impossible?
10:40: *Coffee*
11:00: **Ann Russell**: New insights on the incorporation of geochemical carbonate ion proxies into foraminifera
11:40: **Yair Rosenthal**: Orbital- and millennial-scale variations in the global carbon cycle
12:30: *Lunch*
13:30: **Nick Shackleton**: The role of carbon dioxide in the ice age cycles
14:20: **David Lea**: Tropical Temperature Leads on Glacial Terminations
15:10: **Howard Spero**: Carbon isotope linkage between the tropics and the Southern Ocean during glacial terminations
16:00: **Ernst Maier-Reimer**: Some modelling aspects.
16:40: *Coffee / refreshments / Discussions*
17:10: departure to the new Science Center “*Universum*” in Bremen (17.30-19.30)
19:30: *conference dinner.*

September 3 (plenary session):

- 9:00: **Jelle Bijma**: Overview of EU proposal “6C”
9:30: **Truls Johannessen**: Overview of EU proposal Endici:
10:00: **Anders Lindroth** (ESF representative): best practice to prepare ESF Scientific Programmes or Networks
10:30: *Coffee*
11:00: **Howard Spero**: Summary of yesterdays plenary session and challenges for the working group discussions
11:15: Introduction of the WG themes by the discussion leaders:
 1. Ocean Carbon Isotope dynamics (**DL**: Howard Spero; **R**: Truls Johannessen)
 2. Biological pump and nutrient dynamics (**DL**: Viktor Smetacek; **R**: Frank Peeters)
 3. Reconstructing and modeling past ocean carbonate chemistry (**DL**: Jonathan Erez ; **R**: Bärbel Hönisch)
 4. SST, ice-volume and CO₂: linkages, leads and lags (**DL**: David Lea; **R**: Jelle Bijma)
12.30: *Lunch*
13.30: Working groups convene
16:00: *Coffee*
16:30: Working groups convene
18:30: *Dinner*
20:00: **Jonathan Erez**: video and presentation of experimental work on the calcification mechanisms of *Amphistegina lobifera* (benthic foraminifera)

September 4:

9:00: Working groups convene

10:30: *Coffee*

11:00: Working groups convene

12:30: *Lunch*

13:30: Plenary session: Rapporteurs present working group output (ca. 15 min each) and general discussion

18:30: *buffet*

September 5-7:

A few people stayed to write an outline proposal for a EUROCORE

4. Assessment of the results, contribution to the future direction in the field

One of the objectives of this workshop was to establish state-of-the-science and directions for the paleoceanography community to explore in the future. Towards this goal recommendations have been provided in the three working group reports (see under 2. scientific content). Another contribution to the future direction in the field evolved during the workshop when the ESF representative Anders Lindroth indicated that the Standing Committee for Life & Environmental Sciences (LESC) encourages submission of outline proposals for potential EUROCORE programmes. During the final two days of the workshop, a small group of participants stayed to prepare an **outline proposal for EUROCLIMATE**:

Our ability to predict (anthropogenic) climate change under global warming is limited by the lack of a mechanistic understanding of natural climate variability that is recorded in paleo-records. The proposed EUROCLIMATE answers to these needs, generates the required critical mass, is timely and, is (socio-economically) relevant as it addresses one of big questions of our time: “How will our future climate change?”.

On glacial-interglacial (G-IG) time scales, orbital forcing alone cannot explain the observed changes in climate. The scientific community agrees that the carbon cycle seems to mediate between the relatively weak orbital forcing and strong climate responses, via positive and negative feedbacks that are currently not yet understood. The controls are most probably hidden in a re-organisation of the major carbon reservoirs, which determine atmospheric $p\text{CO}_2$.

The dynamics of the major global carbon cycle reservoirs (marine, terrestrial and atmospheric) are recorded in different geological archives that provide information on the natural system. On G-IG time scales, atmospheric $p\text{CO}_2$ is controlled by the carbonate chemistry of the surface ocean which is “forced” by a reorganisation of the major carbon reservoir inventories (dominated by the carbonate chemistry of the deep ocean). In order to understand the communication between the ocean carbon cycle and climate change, the climate archives of the atmosphere, the terrestrial and the oceanic systems need to be locked into one common timeframe, to detect leads and lags (causes and effects).

To understand climate change on orbital time scales, requires a global understanding of higher frequency (millennial-scale) variability as well. It is therefore absolutely essential to create a global stratigraphy for millennial-scale variability if we are to understand G-IG climate dynamics.

To deconvolve the positive and negative feedbacks between the global carbon cycle and climate change, the physical, chemical and biological parameters that characterize the glacial and interglacial state of the earth as well as the transitions between them need to be determined. In other words, to investigate the controls of the climate system, we need to understand climate sensitive processes in terms of biology, chemistry and physics. This requires a multidisciplinary approach.

During our working group and plenary discussions, the need was identified for an integrated effort to address pertinent questions regarding climate variability on different time scales (G-IG, millennial, anthropogenic). Consensus was reached that in order to achieve a

breakthrough in our understanding of how the natural climate system operates we need to focus on the following objectives:

1. Obtain high resolution, multiple proxy records from atmospheric (ice cores), terrestrial and ocean archives (lake and ocean records).
2. Develop a common chronology for paleo-records of marine and terrestrial and atmospheric archives in order to determine leads and lags (causes and effects). The master chronology should be tuned to high resolution ice-core records.
3. Investigate the dynamics of the carbonate chemistry of the ocean on G-IG time scales as a means to document the integral changes of the global carbon cycle that determine atmospheric $p\text{CO}_2$.
4. Investigate the dynamics of $\delta^{13}\text{C}_{\text{DIC}}$ of water masses in relation to carbon budgets (surface and deep oceans, air-sea interactions, decoupling of $\delta^{13}\text{C}_{\text{DIC}}$ and nutrients)
5. Develop new and (re)calibrate established proxies (going from empirism to a mechanistic understanding)
6. Use modelling tools to test ocean circulation, biological pumping and carbon chemistry scenarios suggested by the paleo-records (modelling applies to the first 5 objectives and is implemented in the text).

These objectives have been worked out in detail in the outline proposal which has been submitted to LESC.

5. Statistical information on the participants

a) Gender

male
28

female
6

b) Countries

Germany
15

The Netherlands
4

USA
6

United Kingdom
3

France
1

Belgium
1

Norway
1

Sweden
1

Russia
1

Isreal
1

c) age structure

26-30
2

31-35
7

36-40
6

41-45
9

46-50
3

51-55
4

56-60
1

61-65
2

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