at New Jersey led the CIE by several thousands of years (but lagged the onset of the *Apectodinium* acme) (Sluijs et al., 2007b). This indicates that warm SST was not the only environmental control on *Apectodinium* abundances. Moreover, it suggests that the carbon burp that caused the CIE was a result of initial climate change and acted as a positive feedback. This scenario fits the model that CH_4 release from submarine hydrates caused the CIE (Dickens et al., 1995). If this pre-CIE warming was global, it was likely induced by greenhouse forcing, suggesting that the PETM warming and ocean acidification were caused by at least two sources of carbon (Sluijs et al., 2007b).

Concluding remarks

The past years of research on the PETM and the more recently discovered additional hyperthermals have resulted in a clearer picture of these critical phases in Earth's history. Improved drilling techniques (Integrated Ocean Drilling Program) have resulted in the recovery of complete sections, and new analytical techniques have contributed to much better quantitative estimates of SSTs. Moreover, high-resolution studies on expanded marginal marine sequences have identified leads and lags in the interaction between the climate system and the carbon cycle during the onset of the PETM. The new data provide fundamental constraints for modeling global climate and carbon cycling, and are increasingly leading to an improved description and understanding of the state and dynamics of a (in this case the early Paleogene) greenhouse world.

Acknowledgements

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Pleistocene records of marine carbonate chemistry

Bärbel Hönisch[1], J. Yu[2] and N.G. Hemming[3]

[1]Lamont-Doherty Earth Observatory, Palisades, USA; hoenisch@ldeo.columbia.edu
[2]Cambridge University, UK
[3]Queens College, Flushing, USA

Ice core records provide the only direct archive for past atmospheric gas composition, and records spanning the past 670 kyr BP reveal a tight correlation between surface temperatures and atmospheric pCO_2 (Petit et al., 1999; Siegenthaler et al., 2005). However, what determines the glacial and interglacial pCO_2 extremes (i.e., 280 vs. 200 ppm), and where the CO_2 was stored is poorly understood, although it is clear that the ocean is the only reservoir that could have absorbed the missing CO_2 from the atmosphere (Broecker, 1982). This uncertainty hampers the prediction of future climate change with continued anthropogenic release of CO_2, and there is a pressing need to better understand the interplay between atmospheric pCO_2 and the much larger oceanic carbon reservoir.

There are several proxies for reconstructing marine carbonate chemistry, all of which have limitations (see Hönisch and Hall, 2007). Although the uncertainties may be large, multiproxy approaches for the late Pleistocene yield an increasingly consistent picture. Paleoreconstructions focus on two approaches: (1) To study the sensitivity of climate to greenhouse gas concentrations beyond the limit of ice coring in Antarctica, reconstructions have focused on the past 60 Myr BP (Pagani et al., 1999, 2005; Pearson and Palmer, 2000; Royer et al., 2001). During this period, oxygen and carbon isotope records from benthic foraminifers indicate large climate fluctuations that coincide with perturbations of the carbon cycle (Zachos et al., 2001). (2) To quantify the potential of the ocean as a sink for CO_2, carbonate chemistry reconstructions focus on benthic foraminifers (Marchitto et al., 2005; Sanyal et al., 1995; Yu and Elderfield, 2007). The glacial deep ocean is thought to be the largest carbon reservoir.

Surface seawater carbonate chemistry

As CO_2 is well mixed in the atmosphere and is exchanged at the air-sea interface, knowledge of past sea surface carbonate chemistry can place constraints on past atmospheric pCO_2. Boron isotopic compositions ($\delta^{11}B$) in marine carbonates record past seawater pH (Hemming and Hanson, 1992; Hönisch et al., 2004; Reynaud et al., 2004; Sanyal et al., 1996, 2000, 2001). Laboratory and sediment validation studies have investigated vital shell size and dissolution effects on $\delta^{11}B$ of planktic foraminifers and corals. Symbiont photosynthesis sequesters CO_2 and thereby increases pH in the calcifying environment of foraminifers (Jørgensen et al., 1985; Rink et al., 1998) and corals (Al-Horani et al., 2003). Respiration has the opposite effect. In planktic foraminifers, these effects have significant consequences for the recorded pH (Hönisch et al., 2003). As symbiont-bearing foraminifers appear to grow larger under higher light levels (Spero and Lea, 1993), higher $\delta^{11}B$ of larger shells of the symbiont-bearing foraminifer *Globigerinoides sacculifer* is interpreted to reflect a shallower growth habitat (Hönisch and Hemming, 2004). The largest shells record surface seawater pH, and because these shells are also the least susceptible to dissolution (typically resulting in offsets to lighter isotopic values), Hönisch and Hemming (2004) recommend using large shells for paleoreconstructions.

A 400-kyr record of $\delta^{11}B$ in large *G. sacculifer* shells from an open ocean sediment core in the equatorial Atlantic shows a ~0.18 unit higher glacial ocean pH compared to interglacials (Hönisch and Hemming, 2005). This is consistent with previous results for Pacific and Atlantic surface seawater pH (Sanyal et al., 1995). Corresponding aqueous PCO_2 estimations

showed a remarkable match with the Vostok pCO_2 record (Fig. 1; Hönisch and Hemming, 2005). Hönisch and Hemming are now in the process of extending the surface ocean pH records into the early Pleistocene and eventually throughout the Cenozoic. There are several problems to overcome in this endeavor, including uncertainty of the boron isotopic composition of seawater on time scales longer than 3-5 Myr BP (Lemarchand et al., 2000), unknown species effects, and the need to estimate surface ocean alkalinity or another parameter of the carbon system in addition to pH when estimating PCO_2.

Carbonate chemistry in reef environments changes seasonally with both the productivity of the ecosystem and changes in the currents that carry the open ocean chemistry to the reef. Therefore, since $\delta^{11}B$ in corals reflect local conditions, corals are not suitable archives for approximating global atmospheric pCO_2 (Hönisch et al., 2004; Pelejero et al., 2005).

Foraminiferal B/Ca ratios have been proposed to reconstruct surface seawater pH (Yu et al., 2007). Similar to the boron isotope proxy, B/Ca is based on the equilibrium reaction between boric acid and borate in seawater. Boron isotope studies suggest that borate is the species incorporated into marine carbonates, and the seawater borate concentration increases with pH. A pilot study suggests that B/Ca is strongly dependent on calcification temperature, which could be corrected using Mg/Ca temperature estimates. Application to the paleo-ocean yields a very promising result: pH of the last glacial Southern Ocean was estimated to have been 0.15 units higher and PCO_2 was correspondingly 95 µatm lower than during the Holocene (Yu et al., 2007). This is an exciting new approach that may allow for a much faster sample throughput. However, because carbonate chemistry and temperature in the ocean typically change in unison, culture experiments under controlled conditions in the laboratory are planned to better quantify the effects of pH, temperature, salinity and boron concentration on B/Ca in planktic foraminifers.

Deepwater [CO_3^{2-}]
The first boron isotope study to estimate glacial deep-sea pH used mixed benthic foraminifers and suggested a 0.3 units higher glacial pH in the Pacific and Atlantic oceans (Sanyal et al., 1995). This large pH change translates into a 100 µmol kg^{-1} higher deepwater [CO_3^{2-}], which is inconsistent with sediment records of carbonate preservation. More recent geochemical estimates use benthic foraminiferal
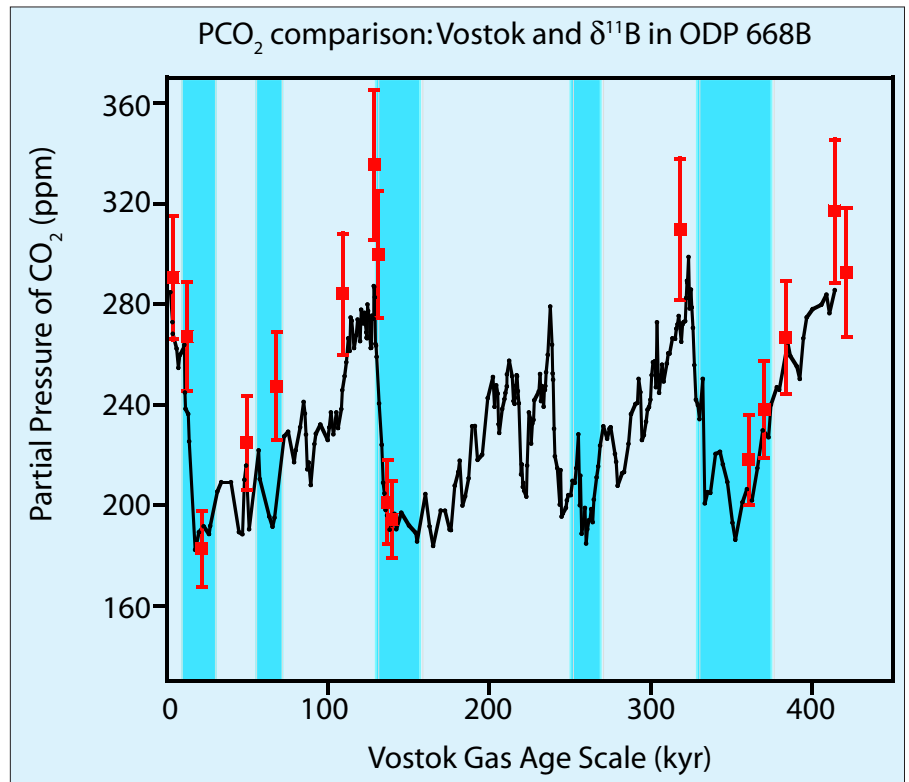

Figure 1: Estimated aqueous PCO_2 from boron isotopes in planktic foraminifera (**red squares**) closely matches atmospheric pCO_2 from the Vostok ice core record (**black line**), and indicates that atmospheric pCO_2 can be estimated from marine proxy records. **Blue bars** indicate glacial intervals. Modified from Hönisch and Hemming, 2005.

Zn/Ca and Cd/Ca (Marchitto et al., 2002), and B/Ca ratios (Yu and Elderfield, 2007), which appear to be related to deepwater carbonate saturation state, although the exact mechanism of the respective relationship is not understood. Reconstructions of [CO_3^{2-}] of the glacial Atlantic was 15-30 µmol kg^{-1} higher at intermediate depths, and ~10-20 µmol kg^{-1} lower in waters below the modern lysocline (water depth where the rate of calcite dissolution increases dramatically) (Farrell and Prell, 1989; Marchitto et al., 2002; Yu and Elderfield, 2007). In the Pacific Ocean, a 5 µmol kg^{-1} increase occurred in waters deeper than 3000 m (Anderson and Archer, 2002).

Because of the large discrepancy between mixed benthic $\delta^{11}B$ data and other reconstructions, Hönisch, et al. (in prep.) measured $\delta^{11}B$ in single benthic foraminifer species, which yield corresponding [CO_3^{2-}] data that show a small glacial increase above the modern lysocline and a small decrease below the lysocline. This brings the boron isotope data in line with other reconstructions and strengthens the view that the deep ocean cannot have stored the entire missing CO_2 in dissolved form. Biological mechanisms must have played an important role as well.

Where to next?
Beyond the need for detailed and faithful estimates of surface seawater PCO_2 and atmospheric pCO_2 throughout the Cenozoic (see above), detailed maps of deep

sea carbonate parameters are needed to better quantify the past oceanic carbon reservoir. Particularly for deep-sea reconstructions, the mechanisms of the proxy relationships need to be studied and better calibrated, preferably in laboratory culture. Depth profiles from different locations in all ocean basins (particularly the Pacific and Southern Ocean) need to be generated, as well as reconstructions through longer periods of time at single locations. This is a long-term endeavor that needs to be approached by the entire paleoceanographic community and not just by single individuals.

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