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Paleo-atmospheric CO_2 reconstructions from deep-ocean sediments

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Biological remains in ocean sediments document the remarkable history of atmospheric CO_2 and its fundamental control on Earth's climate. Higher resolution studies are needed to better understand the short-term processes that inform imminent anthropogenic climate changes.

Human activities have increased the concentration of carbon dioxide in our atmosphere from 280 ppm before industrialization to 424 ppm in 2024. Without reductions in emissions, CO_2 is projected to rise to >800 ppm by the end of this century, driving warming well in excess of the 1°C already recorded (IPCC 2021). How warm it will get can be projected by complex numerical climate models whose skills are validated using the detailed relationship between atmospheric CO_2 and global climate in Earth's history. Instrumental measurements of CO_2 have been collected since 1958 (Lan et al. 2024), and ancient air trapped in Antarctic ice documents Earth's atmospheric composition over hundreds of thousands of years prior (Bereiter et al. 2015; Yan et al. 2019). However, CO_2 of this geologically recent past was generally lower than today, and global temperatures colder. Much warmer intervals occurred in the distant past, but because the atmosphere of that time cannot be sampled directly, paleo-CO_2 reconstructions rely on indirect proxies preserved in the sedimentary record.

Reconstructing CO_2 from ocean sediments

Deep-sea sediments are key to paleo-reconstructions; they are globally distributed and gradually accumulate biogenic and inorganic proxy materials over tens of millions of years, thereby providing excellent age stratigraphy. Uniquely useful in documenting past surface-ocean temperatures and the partial pressure of CO_2 (P_{CO2}) are the mineralized and organic remains left behind by organisms that once inhabited the ancient surface ocean. This is because gas exchange at the air-sea interface drives P_{CO2} in seawater towards equilibrium with P_{CO2} in the atmosphere. Once absorbed in seawater, CO_2 reacts with water (H_2O) and forms a suite of carbon species whose abundances are controlled by well-understood chemical equilibrium reactions that also determine seawater acidity (i.e. pH).

Not all oceanic regions are appropriate for paleo-CO_2 studies because vigorous photosynthesis can diminish sea-surface CO_2 while upwelling of deeper waters delivers respired CO_2 to the surface, disturbing the air-sea equilibrium. Therefore, paleo-CO_2 studies focus on off-shore regions such as subtropical gyres, where photosynthesis is weak and downwelling of surface waters allows air-sea equilibrium to be established.

There are two main frameworks for marine-based CO_2 reconstructions: the stable carbon isotopic composition of organic phytoplankton ($\delta^{13}C_{phytoplankton}$) remains and the boron isotopic composition ($\delta^{11}B$) of fossilized $CaCO_3$ shells. Briefly, the $\delta^{13}C_{phytoplankton}$ proxy assumes CO_2 passively diffuses into an algae cell, and the CO_2-fixing enzyme Rubisco preferentially takes up ^{12}C over ^{13}C during oxygenic photosynthesis. When CO_2 is abundant, ^{12}C is preferentially incorporated into organic matter (resulting in relatively lower $\delta^{13}C_{phytoplankton}$). The opposite occurs at low CO_2 (Fig. 1). Although first applied to bulk organic matter (Popp et al. 1989), selective preservation and mixed organic sources imposed problems. These challenges have been resolved by using (1) specific compounds produced by select algae (e.g. alkenones from Haptophytes), (2) specific compounds produced by the broader phytoplankton community (e.g. chlorophyll), enabling greater spatial and temporal diversity of reconstructions, and (3) organic carbon bound to mineral or organic exteriors of e.g. coccolithophores, diatoms or dinoflagellates. The detailed systematics of these approaches are reviewed in Hollis et al. (2019).

The boron isotope proxy measured in planktic foraminifer shells is sensitive to seawater-pH rather than directly to P_{CO2}, but seawater-pH and P_{CO2} are closely related. Briefly, the concentration and isotopic composition of borate ions ($B(OH)_4^-$) in seawater decrease with decreasing pH (and increasing CO_2). During foraminiferal growth, a small number of borate ions ($B(OH)_4^-$) substitutes for carbonate ions ($CO^{3}{}_2^-$) in the $CaCO_3$ shell. The isotopic composition ($\delta^{11}B_{borate}$) of dissolved borate decreases with decreasing pH; therefore, foraminiferal $\delta^{11}B$ also decreases, and vice versa at high pH (Fig. 1). Calculating P_{CO2} from pH requires knowledge of a second parameter of the marine carbon system (ideally, total alkalinity or the total concentration of dissolved inorganic carbon, DIC). The detailed systematics of this proxy have recently been reviewed (Rae et al. 2021).

The Cenozoic record of atmospheric CO_2

The recent publication by $CenCO_2PIP$ Consortium (2023) on paleo-atmospheric CO_2 highlights the role of this gas in regulating Earth's temperature over the past 66 Myr, and the critical role of ocean drilling in these findings (Fig. 2). The compilation is constructed from terrestrial and marine CO_2-proxies, but deep-ocean sediments provide much of the temporal continuity and a noteworthy portion of the data. The record demonstrates a long-term decline in atmospheric CO_2 that closely correlates with cooling from the Eocene "hot-house" to the Pleistocene "ice-house", interspersed by

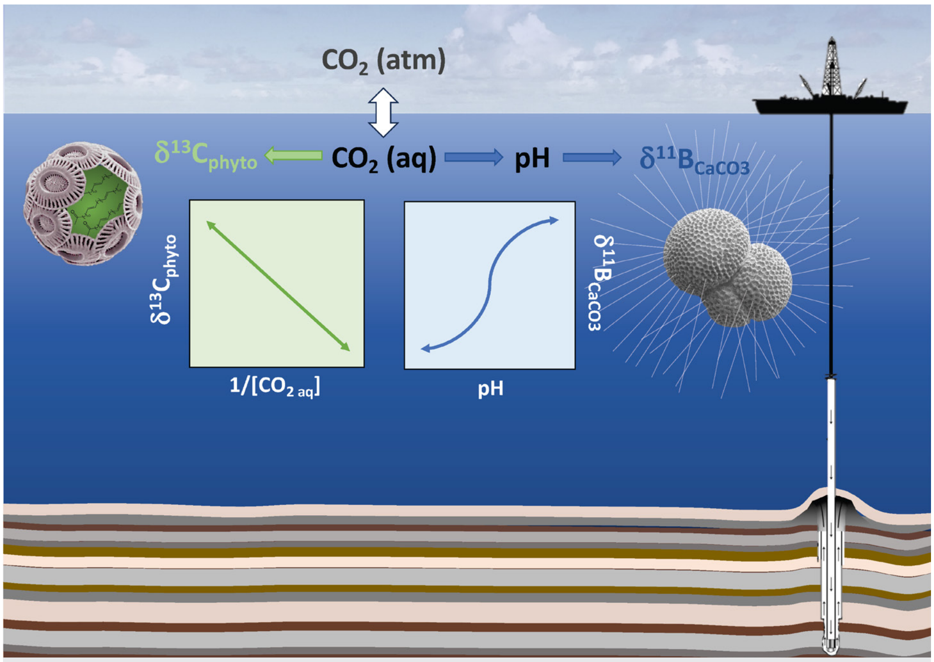

Figure 1: Basic systematics of the two marine CO_2 proxies. Fossil organic compounds and $CaCO_3$ shells are preserved in layered ocean sediments that can be extracted by deep-aocean drilling.

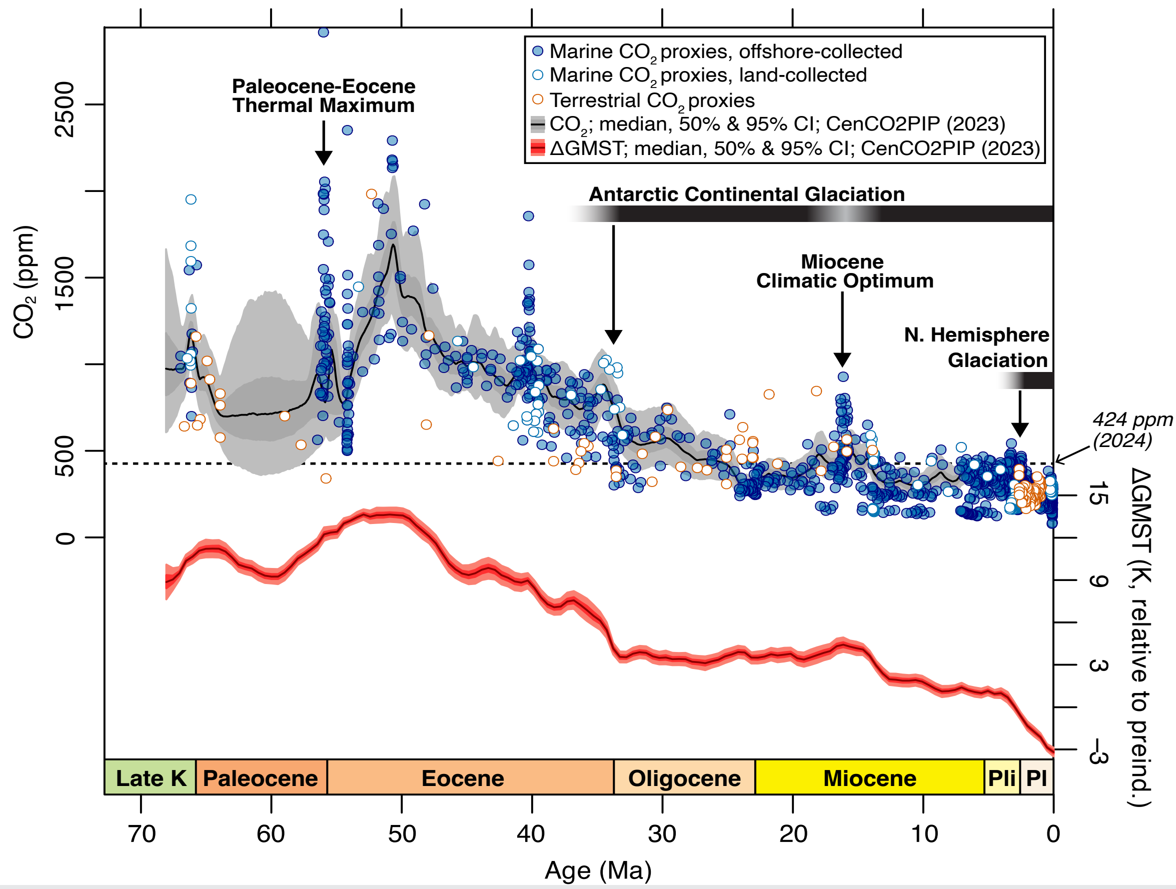

Figure 2: Cenozoic CO_2 proxy data and statistical reconstruction (CenCO2PIP Consortium 2023), and Global Mean Surface Temperature anomaly (500-kyr mean values) relative to pre-industrialization (after Westerhold et al. 2020).

several prominent climate events. The first is a prominent peak in CO_2 at the Paleocene-Eocene Thermal Maximum (PETM) that drove dramatic warming, ocean acidification, intensified storms and climate extremes (McInerney and Wing 2011). This, and other Eocene "hyperthermal" events, provide the most direct paleo-analogs for ongoing warming from human burning of fossil fuels (Hollis et al. 2019). The second is the establishment of a continent-wide ice sheet on Antarctica at ~34 Myr ago, when atmospheric CO_2 dropped below ~720 ppm. Tectonics and ocean circulation likely preconditioned this event, with a final threshold crossed as atmospheric CO_2 continued to decrease. The third is a rise in atmospheric CO_2 leading to the Miocene Climatic Optimum, the warmest interval in the past ~30 Myr and the last time long-term CO_2 was as high as today. Finally, Northern Hemisphere Glaciations began ~2.7 Myr ago, when proxies suggest that long-term atmospheric CO_2 declined to 270 ppm. Further climatic and biotic features associated with these CO_2 changes are detailed in CenCO_2PIP Consortium (2023).

Future outlook

Most paleo-proxies we use today have only been developed and/or significantly improved over the past few decades. Scientists are still looking for proxies to quantify additional parameters of the marine carbonate system, the changing elemental and isotopic composition of seawater and atmosphere, and opportunities to leverage the largely unexplored abyssal seafloor that is poor in, or even devoid of, $CaCO_3$ fossils. Legacy sediment cores provide important resources to make further advances, but one that is ultimately limited. For instance, some of the most important sections, such as the PETM, are largely depleted in existing sediment cores. Increasing the temporal resolution of paleorecords and extending them temporally and spatially requires drilling new cores.

Many paleo-CO_2 reconstructions have focused on brief events and major transitions in Earth's climate history, leaving much of the geologic record sparsely sampled. This leaves large uncertainties during intervals such as the Paleocene and Cretaceous, but also the Oligocene, when marine proxies suggest decreasing atmospheric CO_2, but paleo-temperature estimates are mostly flat (Fig. 2). Filling these gaps and constraining paleo-CO_2 variability on orbital cycles (i.e. 10–100 kyr) will increase confidence in our understanding of the climate system. Critically, such studies will provide important constraints on the natural processes that will ultimately help neutralize anthropogenic emissions. These studies will benefit from new computational tools like forward proxy system models (Bowen et al. 2020; Evans et al. 2013), which facilitate the combination of proxy estimates, a more robust statistical assessment of uncertainties, and new opportunities to explore the individual controls of different proxies.

In summary, the international collaborations facilitated by the International Ocean Discovery Program and its legacy programs have laid the foundation for community consensus studies like CenCO_2PIP. Much work remains to be done on sediment cores collected over the course of these programs, but continuing the pace of knowledge gain and opening new frontiers in paleoclimate exploration will ultimately require the acquisition of new open ocean sediment archives.

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Investigation of orbital and sub-orbital Milankovitch cycles from borehole logging data: Examples from Cretaceous and Quaternary lake sediments

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Lake records hold valuable information on orbital forcing and local climate feedback. Physical property datasets from lakes can be established through borehole logging, which are able to record sub-orbital signals such as half-precession.

Borehole measurements: A fast method to obtain physical properties of lacustrine sediments

Studies of lake sediment are an important part of environmental and geological sciences. They provide an indispensable contribution for the sediment-based reconstruction of past environmental conditions on the continent, and also allow for studies of present-day environmental processes and challenges over a longer time perspective. In particular, the analyses of drill-core samples can indicate substantial climatic variations over the past hundreds to thousands of years. Moreover, they facilitate important insights into changes in vegetation, lake-level history and rates of sediment accumulation that are usually more rapid in lakes than in marine environments (Cohen 2003).

The type of sedimentation and geophysical properties of lacustrine lithological units can be investigated with different measurement techniques on core material and by borehole measurements, known as downhole logging (see e.g. Rider and Kennedy 2011 for an overview). However, these datasets are rarely used in lacustrine projects.

Downhole logging is usually carried out directly after coring, and is a powerful and universal method that provides continuous records of the physical, chemical and structural properties of sediments and rocks surrounding a borehole, such as natural radioactivity, electric resistivity, density, porosity, and magnetic susceptibility. The data characterize the properties of drilled lithologies, and can fill gaps resulting from incomplete core recovery.

In lacustrine drilling projects, insitu borehole measurements allow for recording climatic changes and reconstructing the cyclic characteristics of the respective sediments. Variations in sediment properties are often based on climatic changes (e.g. Baumgarten et al. 2014; Ulfers et al. 2021; Zeeden et al. 2023). Specific values, ratios and correlations of e.g. gamma ray radiation and magnetic susceptibility can be interpreted to represent specific lithologies (e.g. Sardar Abadi et al. 2022 and references therein). To obtain a quantified overview of a multi-proxy logging dataset, often cluster analysis is used. It represents a powerful method to determine depth intervals with similar properties, which then can be interpreted in a lithological, paleolimnological and paleoclimatic context.

Milankovitch forcing and nonlinear climate feedbacks detected through downhole logging

Cyclostratigraphic studies focus on the identification, characterization and interpretation of quasi-cyclic variations in stratigraphic records and their application in geochronology (e.g. Hilgen et al. 2015) using astronomical cycles of known periodicities (eccentricity, obliquity and precession of the Earth´s movements), known as Milankovitch cycles.

Milankovitch cycles describe the effects of changes in the Earth's astronomical and orbital variations on our climate system on scales from tens of thousands to millions of years. Eccentricity, obliquity and precession drive quasi-cyclic variations in the time variant latitudinal distribution of solar radiation at the top of Earth's atmosphere. This periodic orbital forcing strongly influenced Earth's climate, and can influence oceanographic, sedimentary and biological changes that are potentially recorded in the sedimentary archives through geologic time. This response can be imprinted as variations

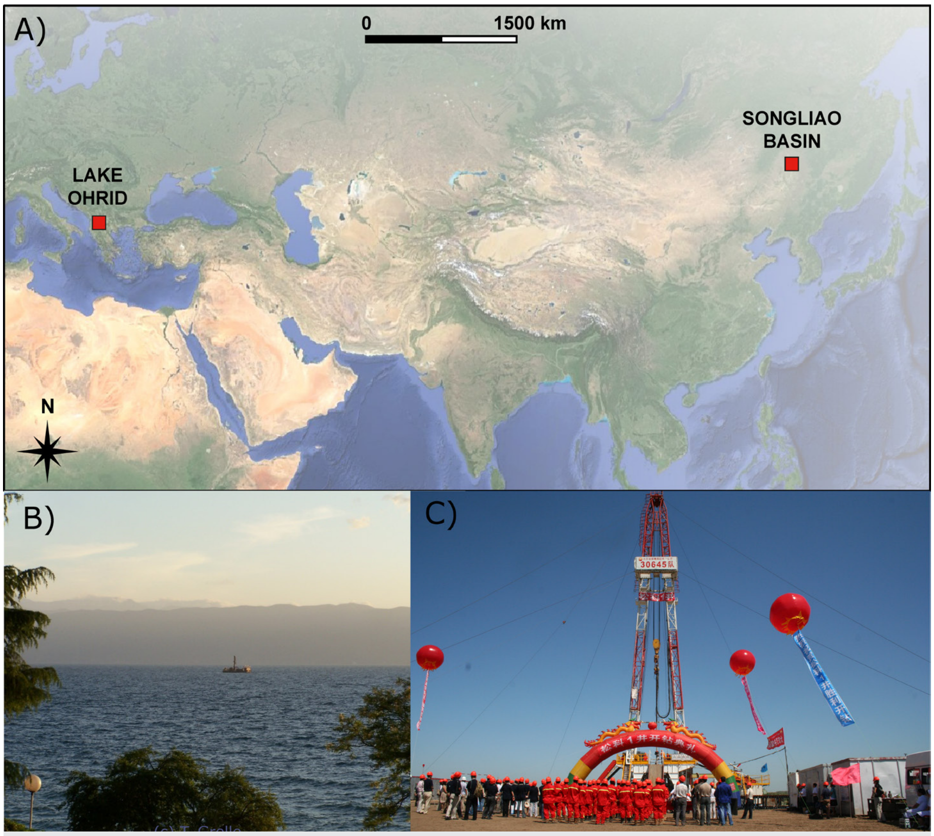

Figure 1: (A) Location map of the Songliao Basin (China) and Lake Ohrid (Albania/North Macedonia - Balkan Peninsula) localities – both drilled in the frame of ICDP. **(B)** Image of the Lake Ohrid Drilling Camapign, and **(C)** the Songliao drilling project.