

## 8B.4 A PERSPECTIVE ON CLIMATE AND MARINE BIOGEOCHEMISTRY (OCEAN ACIDIFICATION) CHANGE FROM PALEO PROXY EVIDENCE

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### 1. Introduction

Evidence from paleo proxies such as marine sediments and coral reefs provides a valuable perspective on past changes in climate and marine biogeochemistry. Climate and marine biogeochemical changes are linked on many different timescales, because changes in climate affect ocean chemistry, and changes in ocean chemistry, notably the carbon dioxide concentration of the surface ocean, affect climate. Improving our understanding and developing a predictive ability with regard to these feedbacks will improve our ability to predict future climate change.

Recently developed proxies for seawater carbonate chemistry are revolutionizing our understanding of the climate-ocean carbon link (Anderson, et al., 2009). A small amount of carbon dioxide exists in the surface ocean in a gaseous form (aqueous  $\text{CO}_2$ ). Most of the  $\text{CO}_2$  that enters the ocean dissolves in seawater to form carbonic acid, which dissociates to form hydrogen ions ( $\text{H}^+$ ) (lowering the pH), carbonate ions ( $\text{CO}_3^{2-}$ ), and bicarbonate ions ( $\text{HCO}_3^-$ ). Certain trace metals and stable isotopes are sensitive to the concentrations of these ions and are preserved in sediments and skeleton remains, allowing the concentrations to be reconstructed through time. The boron stable isotope ratio preserved in foraminifer plankton shells is sensitive

to pH. The concentration of several trace metals that are incorporated into calcium carbonate skeletons, including U/Ca, Zn/Ca, and B/Ca, are sensitive to the carbonate ion concentration. The stable isotopes of carbon in organic matter,  $^{13}\text{C}$  and  $^{12}\text{C}$ , vary with the concentration of aqueous carbon dioxide. Although complications exist, the carbon isotope proxy has been used to reconstruct aqueous  $\text{CO}_2$  and effectively confirms that seawater concentrations have varied in concert with the atmosphere as expected (Rau, et al., 1991).

Additionally, the saturation state can be reconstructed from the amount of carbonate preserved on the seafloor, and the extent to which different carbonate skeletal remains are preserved. Proxies for the saturation state tend to be crude or qualitative, but provide an essential complement to the chemical proxies. So far, these proxies have been applied to the Glacial-Interglacial cycles that dominated the past few million years, and are beginning to be applied to older time periods. Coupled with proxies for climate, the proxies for seawater chemistry can provide insight to complex relationships and feedbacks and how they have varied through time.

### 2. Past Changes in Climate and Marine Biogeochemistry

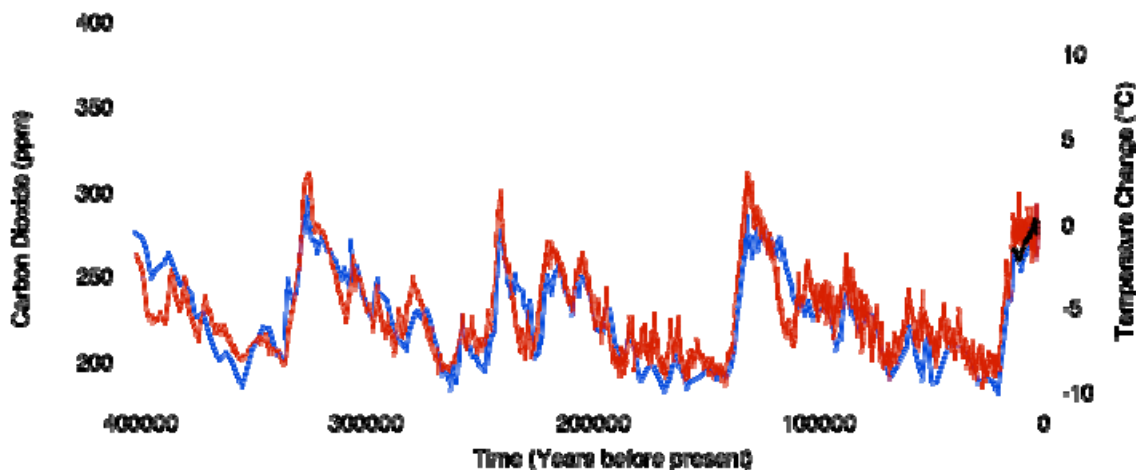


Figure 1. Changes in carbon dioxide concentration in the atmosphere (red) and temperature derived from deuterium in ice cores (blue, black) during the last four glacial cycles (Petit, et al., 1999).

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The Earth's Glacial-Interglacial cycles have occupied the most recent Geologic Period, the Quaternary, spanning the last 2.6 Million years. These cycles vary at periods of 100,000, 41,000, and 21,000 years. The most recent 500,000 years were dominated by the

100,000 year cycles, and reveals a remarkable coincidence between temperature, carbon dioxide (observed in ice cores), and seawater carbonate chemistry (Fig. 1) (Petit, et al., 1999). The ice core record of temperature and carbon dioxide has been known for several decades, but the corresponding ocean chemical changes have only been recently confirmed. The boron isotopic record indicates that the seawater pH varies in concert with climate (Fig. 2) (Hoenisch, et al., 2005). The magnitude of surface-ocean pH change is consistent with a reduction in the aqueous carbon dioxide concentration.

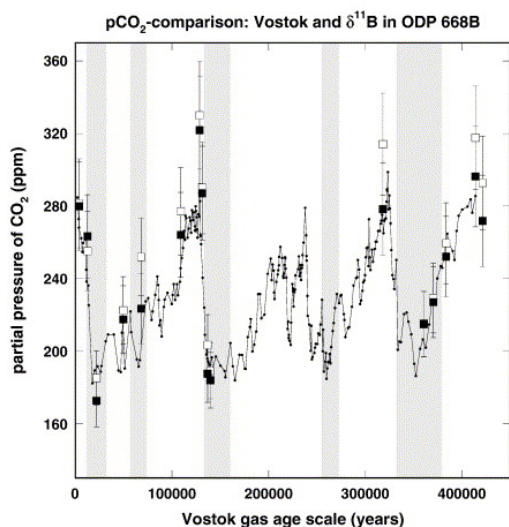


Figure 2. Changes in carbon dioxide concentration in the VOSTOK ice core, and seawater pH during the last four Glacial-Interglacial stages (Hoenisch, 2005). Filled and open circles represent different pH reconstructions, and the gray shading indicates the Glacial periods.

Owing to the equilibrium reactions among carbonate species, the Glacial increase in pH and reduction in aqueous carbon dioxide corresponds to an increase in the carbonate ion concentration, significant because the carbonate ion saturation determines whether skeletal calcium carbonate is preserved or dissolved in the ocean. Compared to the surface ocean, the chemical properties of the deep ocean have been more difficult to reconstruct, and this reconstruction is essential before the climate-carbon connection can be elucidated. One reconstruction (Fig. 3) reveals little change in the deep-sea carbonate ion concentration, but large changes in the surface ocean (Anderson and Zhang, 2009). This is consistent with theories about the ocean's ability to buffer chemical changes, but needs to be confirmed by other proxies. The changes shown in Figure 3 are also consistent with the theory that ocean stratification underlies the change that causes the Ice Ages (Sigman and Boyle, 2002). Increased stratification retains more carbon in the deep sea relative to the surface during the cool Glacial intervals, while during the warm Interglacial periods, reduced ocean stratification makes the two

reservoirs more equal, increasing the amount of carbon in the surface ocean. Today, the ratio of carbon in the surface to deep-ocean is about 1 to 60, most of the carbon existing in the deep ocean as bicarbonate ion.

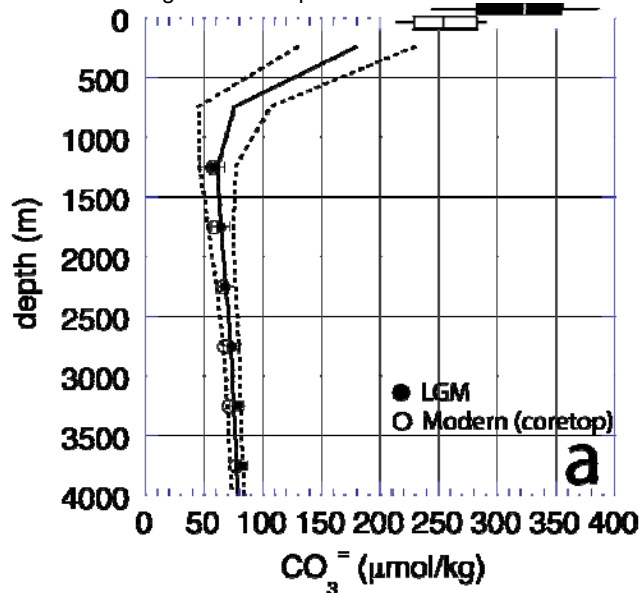


Figure 3. Vertical profile of the carbonate ion concentration in the Pacific for the modern and reconstructed for the Last Glacial Maximum 21,000 years ago. The line is the modern profile and its one standard deviation (dashed), modern reconstructions are the open symbols, and the closed symbols are the LGM reconstruction. The increase at the sea surface is 80 micromoles/kg (Anderson and Zhang, 2009).

Alternate theories attribute the carbon changes to exchange among different reservoirs, including the ocean, atmosphere, and terrestrial biosphere, or to other processes such as high latitude ice cover, but all theories now attempt to explain not only the atmospheric changes but also the surface ocean change.

The Cenozoic Era spans the last 65 Million years (Fig. 4). Proxies such as oxygen isotopes and the presence of floral and faunal remains on land and ocean provide a picture of climate during the Cenozoic, but the carbon cycle changes are not yet well-resolved. Climate was warm during the Early Cenozoic. The higher latitudes were much warmer, reducing the gradient between the low and high latitudes. Cooling occurred throughout the Cenozoic interval, culminating in the coolest interval, the Quaternary, which contains the Ice Age intervals described above. The transition from warm to cold, and the increasing zonal gradient, have been described as a transition from a Greenhouse to an Ice House World, emphasizing the role of the formation of polar Ice Caps during this transition, and also emphasizing theories that attribute the early warmth to increased carbon dioxide (Zachos, et al., 2005). Proxies and reconstructions of the carbon change are still being developed, and a robust picture of the carbon change corresponding to

the temperature change shown in Fig. 4 has not yet been produced.

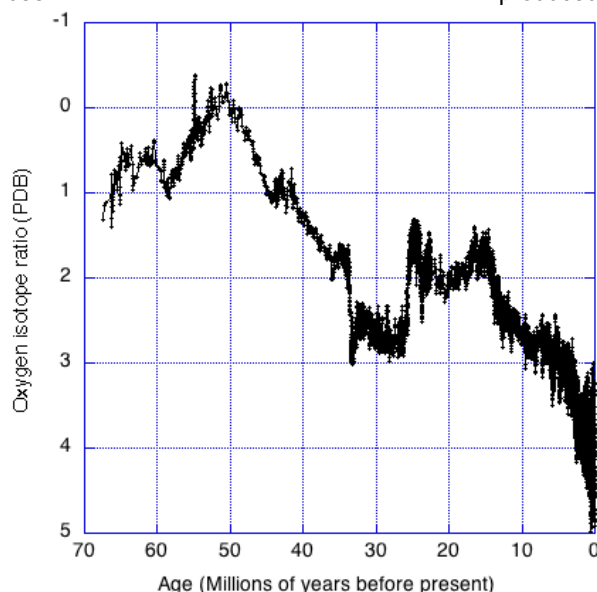


Figure 4. Oxygen isotopes during the last 65 Million Years show warm conditions 50 million years ago, and the cooling that occurred throughout the last 50 million years. The variability of the past 2.6 million years is associated with the Ice Ages. At this scale the Ice Age cycles shows up as a thickening of the black line. The PETM appears as a brief excursion to more negative isotope values about 55 million years ago (Zachos, et al., 2001).

Over millions of years, many different influences can affect the amount of carbon dioxide in the ocean and the atmosphere, including volcanic production, weathering, and removal in deep-sea sediments. A long transient evolution of carbon forced by multiple influences, in turn driving long-term climate change, is not unexpected.

Abrupt climate changes occurred several times during the Cenozoic. One of the largest and best-studied changes, characterized by an abrupt warming followed by an abrupt cooling, occurred approximately 55 million years ago at the Paleocene-Eocene boundary. On Figure 4, the abrupt warming appears small spike 55 million years ago. This event, termed the PETM, was also accompanied by abrupt changes in seawater chemistry, including a dramatic lowering of pH and decrease in carbonate ion saturation (Zachos, et al., 2001). Regions of the ocean became so undersaturated that for a period of tens of thousands of years no calcium carbonate accumulated at the seafloor. Eventually the seawater saturation state returned to a level close to that preceding the event. The PETM provided a concrete example of carbonate compensation, whereby the accumulation and dissolution of carbonate minerals increase and decrease in such a way as to minimize changes in the saturation state.

### 3. Perspective on Future Change

The two best-studied intervals, the Cenozoic and the Quaternary, provide observations highly relevant to future change. The Quaternary Ice Ages show that Earth temperature has varied as the concentration of the carbon dioxide has changed. While the mechanisms driving these changes remain illusive, the correspondence is consistent with a radiative forcing of carbon dioxide equivalent to about 4.4-5.6°C for a doubling of CO<sub>2</sub> (Lea, et al., 2004). Much more can be done to refine the sensitivity obtained from paleo studies, but this estimate is remarkably similar to the sensitivity derived from other means (3°) and used in climate model simulations (IPCC, 2007).

The second observation is that the ocean has the ability over long (10,000 year) time scales to compensate for the carbon dioxide added or removed, so that the concentration in the ocean and the atmosphere remains the same (Archer, et al., 1999). Based on the past, one expects that over thousands of years, nearly all of the carbon dioxide added as the result of human activity will be neutralized by reaction with the skeletal remains that line the seafloor, returning the atmospheric carbon dioxide concentration, and the seawater chemistry to a condition close to the pre-perturbed state.

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