

# Modern CaCO<sub>3</sub> preservation in equatorial Pacific sediments in the context of late-Pleistocene glacial cycles

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## Abstract

The CaCO<sub>3</sub> content of marine sediments in many regions of the ocean has varied systematically with climate throughout the late-Pleistocene glacial cycles. Both biological productivity and carbonate preservation have been proposed to be the master variable regulating this variability. We have evaluated the preserved flux of CaCO<sub>3</sub> in cores from the central equatorial Pacific Ocean (~140°W) using the <sup>230</sup>Th-normalization technique. Neither barite fluxes nor <sup>10</sup>Be/<sup>230</sup>Th ratios, both geochemical proxies for export production, correlate with CaCO<sub>3</sub> fluxes, indicating that productivity is not the principal factor controlling CaCO<sub>3</sub> accumulation in these sediments. Preserved fluxes of CaCO<sub>3</sub> in central equatorial Pacific sediments correlate in time with the benchmark CaCO<sub>3</sub> record from the Cape Basin (South Atlantic Ocean), supporting the view that changes in ocean chemistry (carbonate ion concentration) have controlled the pattern of CaCO<sub>3</sub> preservation and accumulation at these sites. Modern CaCO<sub>3</sub> preservation in equatorial Pacific sediments has dropped to levels nearly as low as those experienced at any time in the late Pleistocene. Similar changes occurred at the end of each of the late-Pleistocene interglacial periods, from which we infer that ocean carbonate chemistry has already undergone changes that are expected to precede the transition into the next ice age. However, during the late Pleistocene, the time interval between the decrease in CaCO<sub>3</sub> preservation and the end of the interglacial has varied substantially from one interglacial to another (from ~2000 to ~15,000 years), so the late-Holocene decrease in CaCO<sub>3</sub> preservation cannot be used to predict the end of the Holocene interglacial period.

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## 1. Introduction

One of the most striking features of the marine geological record is the quasi-regular pattern of variability

in the CaCO<sub>3</sub> content of sediments found in many regions. This pattern was first described by Arrhenius (1952), who noted that maxima and minima of CaCO<sub>3</sub> abundance could be correlated for thousands of kilometers across the equatorial Pacific Ocean. Many subsequent studies have demonstrated that similar patterns occur outside the equatorial Pacific region, for example in the Indian Ocean (e.g., Peterson and Prell, 1985) and in the Subantarctic zone of the Southern Ocean (e.g., Hodell et al., 2001).

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For features as widespread as this, one naturally wants to know when and how the variability in the  $\text{CaCO}_3$  content of sediments was generated, and whether or not the patterns observed in different ocean regions are related to one another. Each of these questions, in turn, leads to more focused inquiry concerning the physical and biogeochemical processes that generated these features.

Consensus was reached long ago concerning “when” these features were formed. Calcium carbonate abundance in sediments of the three regions mentioned above (equatorial Pacific, Indian and Subantarctic Southern Oceans) tends to be at a maximum during late glacial periods and during deglaciation, and at a minimum during times of continental ice sheet growth (e.g., Peterson and Prell, 1985; Farrell and Prell, 1989; Hodell et al., 2001). In contrast to the general agreement concerning the timing of these features, the processes responsible for the variable  $\text{CaCO}_3$  content of sediments (i.e., “how”) have been debated for over half a century (e.g., Arrhenius, 1988; Farrell and Prell, 1989; Archer, 1991; Berger, 1992; Murray et al., 2000). Briefly, the debate centers on the relative importance of biological production of  $\text{CaCO}_3$  versus  $\text{CaCO}_3$  preservation as the master variable regulating the  $\text{CaCO}_3$  content of sediments. Whether control is primarily by production or by preservation, the underlying cause represents a fundamental link between ocean biogeochemistry and climate change. Consequently, the paleoceanographic community has invested a great deal of effort to identify the process(es) responsible.

Evidence in favor of productivity control derives primarily from the apparent co-variation among the accumulation rates in sediments of  $\text{CaCO}_3$  and of other biogenic phases (e.g., opal, phosphorus, organic matter), which tend to be at a maximum during glacial periods (e.g., Arrhenius, 1952; Pedersen, 1983; Arrhenius, 1988; Lyle et al., 1988; Archer, 1991). Arrhenius (1988) reasoned that one would not expect the accumulation rates of other biogenic phases to be sensitive to changes in  $\text{CaCO}_3$  preservation, whereas such co-variation would be consistent with control of the  $\text{CaCO}_3$  content of sediments by biological productivity.

Although the reasoning of Arrhenius is valid, the accumulation rates of equatorial Pacific sediments themselves have become a topic of debate (Marcantonio et al., 1996; Thomas et al., 2000; Marcantonio et al., 2001; Loubere et al., 2004; Lyle et al., 2005; Anderson et al., 2006; Francois et al., 2007; Lyle et al., 2007). Specifically, accumulation rates of biogenic phases in equatorial Pacific sediments that are evaluated by normalizing to  $^{230}\text{Th}$  (Francois et al., 2004)

do not exhibit the pronounced glacial maxima that are evident in records generated by traditional stratigraphic methods, in which average mass accumulation rates are evaluated between age control points. If the outcome of this debate favors the  $^{230}\text{Th}$ -normalization method, then the primary evidence supporting productivity control of  $\text{CaCO}_3$  variability will be eliminated.

Calcium carbonate preservation is regulated in large part (although not entirely) by changes in the carbonate ion concentration of seawater. Calcite solubility increases with increasing pressure (depth), although there is substantial uncertainty in the actual pressure dependence of calcite solubility (Broecker and Clark, 2007). Nevertheless, all other factors being held constant, at a depth of 4 km an increase in the carbonate ion concentration of  $12 \mu\text{mol/kg}$  would deepen the calcite saturation horizon by about 1 km (Broecker and Clark, 2007). Evidence in favor of preservation (dissolution) control of  $\text{CaCO}_3$  variability derives primarily from indicators of the degree of dissolution of foraminifera shells ( $\text{CaCO}_3$ ), such as etching, pitting, fragmentation, and the relative abundances of dissolution-resistant versus dissolution-prone species (see review by Mekik et al., 2002). Generally, although not always (LaMontagne et al., 1996), minima in  $\text{CaCO}_3$  abundance are correlated with independent indicators of increased  $\text{CaCO}_3$  dissolution.

In this study we provide evidence that weighs in on the preservation side of the debate. Our findings support the view that changes in ocean chemistry (carbonate ion concentration) represent the primary factor responsible for  $\text{CaCO}_3$  variability. Furthermore, by analogy with past interglacial periods, when increased  $\text{CaCO}_3$  dissolution preceded the build-up of continental ice sheets, the late-Holocene increase in  $\text{CaCO}_3$  dissolution in equatorial Pacific sediments (e.g., Keir and Berger, 1985; Berelson et al., 1997) suggests that ocean chemistry has already made the change that would precede the earth's transition into the next ice age.

## 2. Study area, cores, and stratigraphy

Cores used in this study were collected during the US Joint Global Ocean Flux Study (JGOFS) Equatorial Pacific Process Study along a transect normal to the equator at  $\sim 140^\circ\text{W}$  (Fig. 1, Table 1). Radiocarbon dates (Table 2) from bulk  $\text{CaCO}_3$  were used to establish age models for the multicores (MC), and for the upper part of the record from each of the gravity (GC) and piston (PC) cores. Oxygen isotope stratigraphies developed using benthic foraminifera are

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