

A decreased carbonate pump during the Oligocene–Miocene transition: Regulating the oceanic buffering capacity

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The ocean carbonate pump plays a crucial role in the buffering effect by regulating the ocean total alkalinity (TA) and dissolved inorganic carbon (DIC). Recent studies suggest that through the Cenozoic the TA and DIC inventory remained relatively constant despite significant changes in continental weathering and $p\text{CO}_2$ variations. Nevertheless, this conclusion is under debate because biogenic calcification (e.g., coccoliths) may have controlled the carbonate precipitation more than the seawater saturation state. During the late Oligocene to the Early Miocene, a decline in $p\text{CO}_2$ is thought to be responsible for Antarctic glaciation, possibly through a threshold effect of ~ 400 ppm, a level we are approaching today. The mechanism(s) that caused this long-term decline in $p\text{CO}_2$ during this period remain(s) an open topic in which fluctuations in the carbonate pump are rarely discussed.

Coccolithophores contribute as much as 90% of the carbonate production and over half of the carbonate sedimentation in the modern ocean. We reconstructed the changes in volume and flux of pelagic carbonate, specifically using *Neolaerhabdaceae* coccoliths. Our investigation spanned the transition from the Paleogene to the Neogene (~ 24 – 20.5 Ma), using marine sediment samples retrieved from International Ocean Discovery Program (IODP) Sites U1501 and U1505 located in the western tropical Pacific Ocean. A circular polarized light microscope was used to measure the thickness/volume of the calcite crystals. Our results show that coccolith thickness or k_s (= volume/length³) decreased from ~ 0.09 during the late Oligocene to ~ 0.06 in the Early Miocene. The k_s value is positively correlated with the bulk sediment carbonate content ($p < 0.01$, $R^2 = 0.5$). We also found that the fine fraction ($< 10 \mu\text{m}$) carbonate stable carbon and oxygen isotopes indicate that there was maximized primary productivity and carbonate dissolution at around 23.5–22.5 Ma. We estimate that coccolith production was ~ 0.15 – 0.50 g carbonate/kyr/cm², which corresponds to ~ 15 – 56% total carbonate flux at the study sites. Scanning electron microscope (SEM) observations revealed that ~ 5 – 30% of coccolith carbonate was dissolved during sinking. The concurrent peaks of primary productivity and carbonate dissolution intensity indicate that organic carbon respiration may have enhanced coccolith dissolution. We propose that the decline in the carbonate pump weakened the removal of TA from the ocean's surface to its depths. Consequently, the enhanced buffering capacity of the ocean likely played a role in the drawdown of $p\text{CO}_2$ from the late Oligocene to the Early Miocene.