The relationship between the carbonate counter pump and seawater CO_2 in the Middle Miocene

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To understand the relationship between the carbonate counter pump and seawater CO_2 in the Middle Miocene between 15 and 12 Ma, samples from International Ocean Discovery Program (IODP) Site U1505 in the South China Sea were analyzed for calcareous nannofossils and organic geochemistry. These included statistical analysis of the absolute abundance of calcareous nannofossils, morphological parameter measurements of Noelaerhabdaceae, alkenone and glycerol dialkyl glycerol tetraether (GDGT) lipid content, and alkenone stable carbon isotope composition. The conclusions are as follows:

(1) The length, thickness, and mass of Noelaerhabdaceae, *Helicosphaera* spp., and *Coccolithus pelagicus* show relatively similar variation trends. There is a significant correlation between the length and thickness of Noelaerhabdaceae coccoliths. The calcification index calculated by morphological parameters shows that the calcification of coccoliths experienced three peaks starting from 15.2 Ma that reached a maximum value at the end of the Middle Miocene Climate Transition (MMCT).

(2) The stable carbon isotope composition of alkenones in our samples and the calculated fraction value εp of coccolith photosynthesis decreased significantly during the MMCT. These two values are generally greater before the MMCT than after the MMCT, which is the same trend found in benthic foraminiferal oxygen isotopes and global sea level change. The pCO_2 reconstruction using alkenones ranges from 429 to 598 ppm between 15 and 12 Ma. Overall, the pCO_2 values fluctuated but also showed a decrease of about 120 ppm across the MMCT.

(3) The relationship between calcification of coccolithophores and seawater CO_2 was inconsistent before and after the MMCT. Between 15 and 13.9 Ma, coccolith calcification changes correlate with CO_2 values, whereas from 13.9 to 12 Ma, coccolith calcification changes are inversely related to CO_2 values, suggesting that CO_2 is not the main driver of coccolithophore calcification. On the other hand, the mass accumulation rate of coccoliths is an indicator of the strength of the coccolith carbonate pump, and the deposition of coccoliths can affect regional seawater CO_2 values. Calcification and abundance of Noelaerhabdaceae and benthic foraminiferal carbon isotopes change synchronously. Coccolithophore blooms correspond to high values in benthic foraminiferal carbon isotopes, when the marine surface biological pump was weak. This may indicate that there was competition for ecological niches between coccolithophores and diatoms or other algae.