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Calcium carbonate pump during Quaternary glacial cycles in the South China Sea

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Abstract **The preservation and dissolution of calcium carbonate (namely calcium carbonate pump) controls the pH of seawater in global oceans by its buffer effect, and in turn plays a significant role in global changes in atmospheric CO_2 concentration. The results from measured carbonate contents over the past 2 Ma at ODP Site 1143 in the South China Sea provide high-resolution records to explore the process of the calcium carbonate pump during Quaternary glacial cycles. The results indicate statistically that the highest carbonate accumulation rate leads the lightest $\delta^{18}O$ by about 3.6 ka at transitions from glacials to interglacials, and that the strongest carbonate dissolution lags the lightest $\delta^{18}O$ by about 5.6 ka at transitions from interglacials to glacials. The calcium carbonate pump releases CO_2 to the atmosphere at the glacial-interglacial transitions, but transports atmospheric CO_2 to deep sea at the interglacial-glacial transitions. The adjustable function of the calcium carbonate pump for the deep-sea CO_3^{2-} concentration directly controls parts of global changes in atmospheric CO_2, and contributes the global carbon cycle system during the Quaternary.**

Keywords: calcium carbonate pump, biological pump, glacial cycles, Quaternary, South China Sea, Ocean Drilling Program (ODP).

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The most remarkable feature of climate changes during the Quaternary on the Earth is glacial cycles. During cold glacial periods, large continental ice sheets covered much of the polar Northern Hemisphere. During warm interglacial periods, Northern Hemisphere glaciation wanes drastically. The ultimate pacing of these glacial cycles is statistically linked to cyclic changes in the orbital parameters of the Earth, known as the Milankovitch cycles[1]. However, the energy budget effects of the orbital variations are insufficient to drive the large amplitude of the glacial cycles, and orbital variations alone do not provide an obvious cause of the rapid climate transitions evident in geological records. Positive feedbacks within the Earth's climate system must amplify orbital forcing to produce glacial cycles[2]. Among them, the atmospheric CO_2 plays a large role over the glacial cycles[3]. The atmospheric CO_2 concentration has varied in step with glacial-interglacial cycles[4]. During interglacials, the atmospheric partial pressure of CO_2 (pCO_2) is typically near 280 parts per million by volume (ppmv). During glacials, atmospheric pCO_2 is only 180—200 ppmv. The cause of these variations in CO_2 has been a debate on various global change studies, including carbon storage change on land[5], ocean temperature variation[6], calcium carbonate storage change in the ocean[7], ocean nutrition storage change[8], and nutrient utilization at high latitudes[9], but any of them is not broadly accepted[2,10]. Current attention is focused on variations in the atmospheric CO_2 concentration caused by the biological pump[11,12].

The biological pump fixes CO_2 through the photosynthesis of phytoplankton, transports carbon to the deep sea, and results in the temporary or permanent storage of carbon. The biological pump includes two types of carbon pumps[10, 13]: organic carbon pump and calcium carbonate pump (Fig. 1). The organic carbon pump takes up dissolved inorganic carbon (mainly including aqueous CO_2, HCO_3^-, and CO_3^{2-}) and nutrients (essentially phosphate and nitrate) through the photosynthesis of phytoplankton in the euphotic zone (the uppermost 100—200 m), produces organic matter (particulate organic carbon, POC), and releases oxygen. The calcium carbonate pump, however, releases CO_2 through the production of some marine organisms' carbonate skeletons and shells (particulate inorganic carbon, PIC). Most of PIC is the calcium carbonate as calcite and aragonite. Therefore, two types of carbon pumps have different effects on the seawater's carbonate system[10, 13]. In the surface ocean, the organic carbon pump reduces pCO_2, whereas the calcium carbonate pump increased pCO_2. In the deep-sea ocean, a part of organic carbon becomes oxidized, increasing CO_2 (namely respired CO_2), but the dissolution of calcium carbonate takes up CO_2 (Fig. 1).

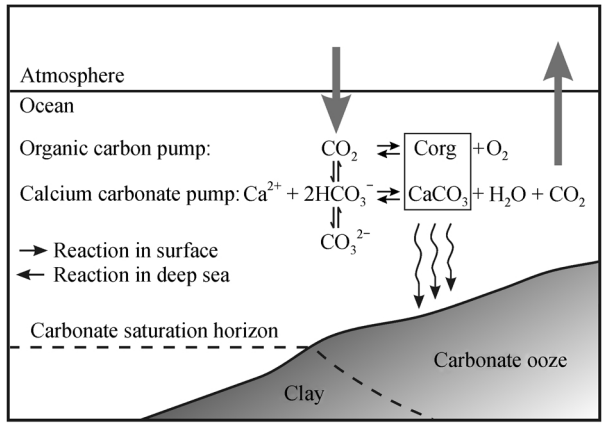

Fig. 1. Aspects of the ocean's biological pump. Dissolved inorganic carbon exists in seawater as aqueous CO_2, HCO_3^-, and CO_3^{2-}. The organic carbon pump is a sink for atmospheric CO_2, whereas the calcium carbonate pump is a source of CO_2 on short time scales. Modified after ref. [10].

Previous studies on atmospheric CO_2 responses of the biological pump were focused on the organic carbon pump, a process fixing CO_2 through the photosynthesis of phytoplankton[8,11,12], but a few efforts were performed on the calcium carbonate pump, a major process controlling the pH of the ocean[10]. The dissolved inorganic carbon as a buffer controls the pH of seawater in global oceans, and in turn plays a significant role to global changes in the atmospheric CO_2 concentration[10,14−16]. The strongest dissolution events, which occurred mainly at transitions from interglacials to glacials during the Late Pleistocene to Holocene, were found firstly at sediment cores in Indian-Pacific Oceans[17,18]. In a study of sediments from the Indian Ocean's 90°E ridge, times of pronounced dissolution happened at the interglacial to glacial boundaries of isotope stages 5/4, 7/6, 9/8, and 13/12 in the past 500 ka[18]. Those events then were confirmed in the deep-sea carbonate sediments in the equatorial Pacific[19,20] and Atlantic[21,22]. Furthermore, the excess $CaCO_3$ dissolution was estimated as about 28 g/cm^2 for each transition event at isotope stages 11/10, 9/8, and 7/6 boundaries in the equatorial Pacific[14]. This result is consistent with those expected from seawater pH shifts reconstructed based on boron isotope measurements and from bottom seawater CO_3^{2-} concentrations measured from foraminiferal shell weight[15]. Therefore, the strong carbonate dissolution events at the interglacial-glacial transitions largely increase the CO_3^{2-} concentration and the pH of the seawater, and in turn force the onset of times of glaciation[14,23]. If strong dissolution events occur at the onset of glacial periods, then one would expect strong preservation events following each termination. Although the preservation event was found at the isotope stages 2/1 transition in the South China Sea (SCS)[24] and in the Late Pleistocene sediments in Indian Ocean[22], perhaps because of the Holocene record being overprinted or the deposition of $CaCO_3$ in coral reefs and shallow banks[14], the investigation of preservation and dissolution events of calcium carbonate (namely calcium carbonate pump) during the Quaternary is far from enough.

The sediment cores at Site 1143 in the southern SCS, recovered during the ODP Leg 184 in 1999[25], reveal high-resolution preservation and dissolution events of calcium carbonate over the past 2 Ma, and provide ideal materials to explore the process of the calcium carbonate pump and its effects on the global carbon cycle system. This paper presents measured results of carbonate contents, carbonate mass accumulation rate, carbonate dissolution index, and benthic foraminifer $\delta^{18}O$, and discusses the process of the calcium carbonate pump during Quaternary glacial cycles in the SCS and its effects on variations in global atmospheric CO_2 concentration.

1 Material and methods

ODP Site 1143 is located at 9°21.72′N, 113°17.11′E, at a water depth of 2772 m in the southern SCS. The core length is 510 mcd (meters composite depth) and displays continuous green or olive green clay, nannofossil, and foraminifer ooze for the upper 100 mcd, and shallower color, decreased green clay, and a few turbidite sediments developed for the lower part[25]. The present depths of the lysocline and the CCD (carbonate compensation depth) in the SCS are about 3000 m and 3800 m, respectively[26,27]. In the last glacial interval, however, the sea level dropped about 116 m[28] and the CCD deepened to 4200 m[29]. Therefore, the materials used in this study are located above the lysocline and CCD. Samples were collected at 10 cm intervals along the upper 95.02 mcd. All samples were analyzed for benthic foraminiferal $\delta^{18}O$, carbonate contents, and fragmentation of planktonic foraminifera.

Oxygen isotope analysis was conducted on the benthic foraminifer *Cibicidoides wuellerstorfi* (300—900 μm size fraction) using a Finnigan MAT 252 mass spectrometer[30]. Data were reported relative to the Pee Dee belemnite standard with an external error of less than $\pm 0.08‰$. The age-depth relationship for Site 1143 was constructed on the basis of precise correlation with the benthic foraminiferal $\delta^{18}O$ from ODP Site 677[31], with a temporal resolution of 2 ka[32]. Carbonate contents were determined using the gasometric techniques[33], which have a precision of better than ±2%. Carbonate mass accumulation rate (MAR) was calculated from linear sedimentation rate, dry bulk density, and carbonate contents[34], in which the dry bulk density was after the shipboard data[25]. Statistics of fragmentation of planktonic foraminifera was took from fractions > 150 μm to reflect various dissolution. The method assuming that each individual foraminifer test breaks up into an average of eight fragments[20] was adopted to calculate the ratio of broken with entire tests. The software Arand[35] was used to conduct cross-correlation analysis between benthic $\delta^{18}O$ and carbonate MAR, and between benthic $\delta^{18}O$ and foraminifer fragmentation, to reveal their general physical-phase correlations. All analyses were carried out at the Laboratory of Marine Geology, Tongji University.

2 Results and discussion

(ⅰ) Variations in carbonate MAR leads fluctuations in $\delta^{18}O$. Values of benthic $\delta^{18}O$ are records of the polar ice volume, reflecting a synchronicity of glacial cycles. The benthic $\delta^{18}O$ results of Site 1143 well correlate to SEPCMAP[36] and other records in global oceans, and thus provide a detailed timescale for the chronostratigraphy of glacial-interglacial cycles[30,32] (Fig. 2). Percentage of carbonate contents varies between 2% and 39%, and their curve is parallel generally to that of benthic $\delta^{18}O$ (Fig. 2), with the highest carbonate content corresponding to the

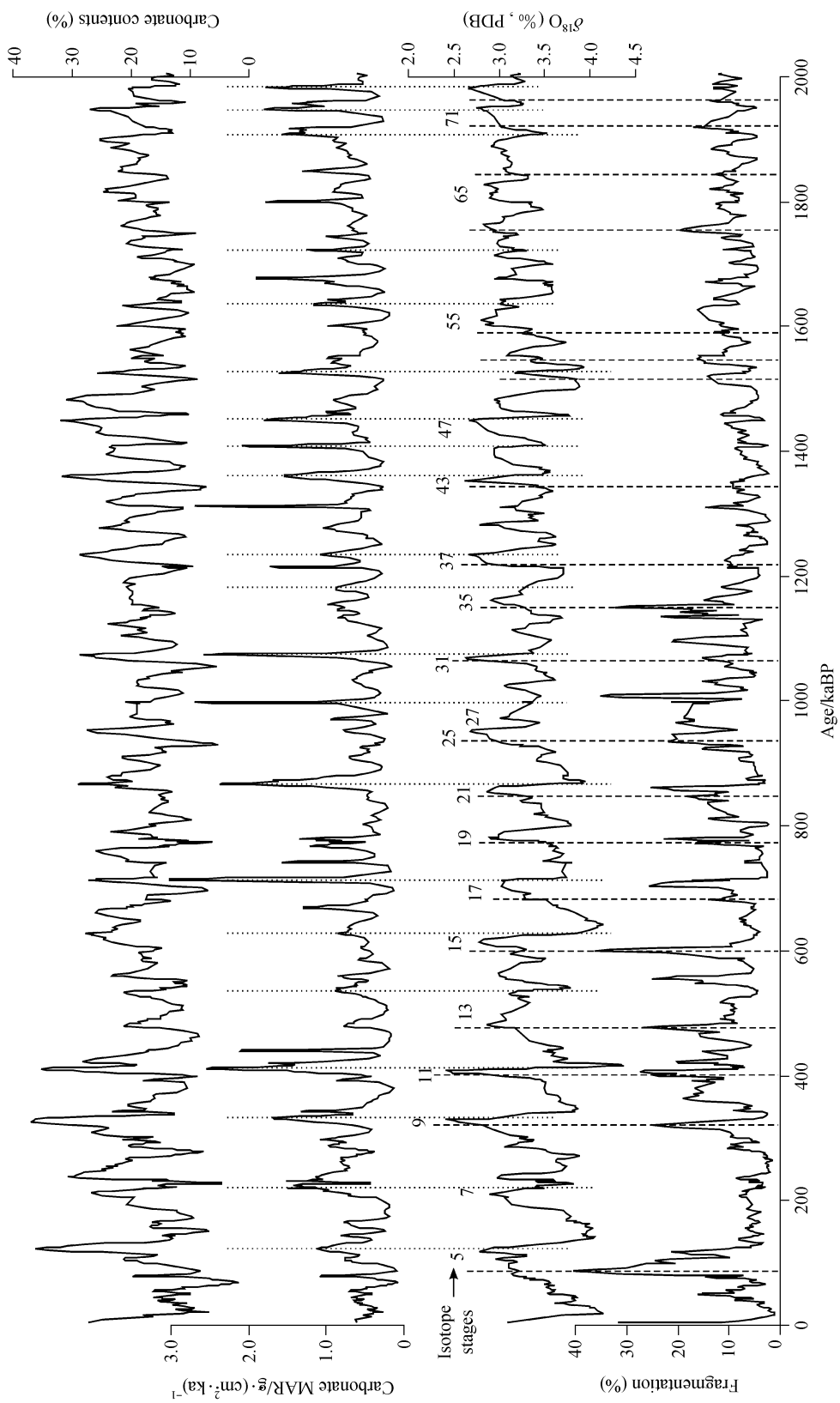

Fig. 2. Carbonate contents, carbonate MAR (mass accumulation rate), benthic foraminiferal $\delta^{18}O$, and planktonic foraminiferal fragmentation over the past 2 Ma at ODP Site 1143 in the SCS. Parallel samples were analyzed with a temporal resolution of about 2 ka. All original data were smoothed with a 3-point running average window. Data of benthic $\delta^{18}O$ and isotope stages after refs. [30, 32].

lightest $\delta^{18}O$. The pattern of the carbonate variability is characteristic of the Atlantic type[21,37], following previous works during the Quaternary in the SCS[38,39]. The carbonate MAR, which is corrected for dilution by terrigenous inputs, can reflect the productivity of calcium carbonate[34] Values of the carbonate MAR at Site 1143 varies generally within 0.2—2.0 $g/cm^2 \cdot ka^{-1}$, with a few values higher to 3.0 $g/cm^2 \cdot ka^{-1}$ (Fig. 2). Note that, the higher carbonate MAR generally occurred at transitions from glacials to interglacials, for examples, isotope stages 6/5, 8/7, 10/9, 12/11, 14/13, and 16/15. Thus may imply significantly increased biogenetic productivity of carbonate shells and nannofossil. Cross-correlation statistical analysis indicates that the best correlation (r = 0.44) of the two signals is obtained if the highest carbonate MAR leads the lightest $\delta^{18}O$ by about 3.6 ka (Fig. 3(a)).

(ii) Variations in carbonate dissolution lags fluctuations in $\delta^{18}O$. Foraminiferal fragmentation usually indicates carbonate dissolution[18,20,34]. The fragmentation at ODP Site 1143 shows periodic dissolution events, with high values up to 40% during strong dissolution events (Fig. 2). These pronounced dissolution events occurred generally at the interglacial-glacial transitions, for examples, isotope stages 5/4, 9/8, 11/10, 13/12, and 15/14, implying increased dissolution during the settling of planktonic foraminiferal shells and from the interaction with hole water on the seafloor. Those results are consistent with carbonate records in global oceans[14,19—22] and from numerical modeling[13]. At the onset of last glacial period, for instance, the CO_3^{2-} concentration in seawater would have risen by 90±30 μmol/L[23]. To obtain this amount of CO_3^{2-} could require the dissolution of 5.3±1.8 g/cm^2 $CaCO_3$ of seafloor, or about 22±8 g/cm^2 of area covered with $CaCO_3$-rich sediments[14]. Cross-correlation statistical analysis confirms that the best correlation (r = 0.42) of the two signals is received if the strongest carbonate dissolution lags the lightest $\delta^{18}O$ by about 5.6 ka (Fig. 3(b)).

(iii) Calcium carbonate pump during glacial cycles. The variations in carbonate MAR lead fluctuations in benthic $\delta^{18}O$, but the variations in dissolution lag benthic $\delta^{18}O$, indicating a potential mechanism of changes in calcium carbonate in seawater during the Quaternary glacial cycles. The results from Site 1143 in the SCS indicate that the carbonate MAR increased at the glacial-interglacial transitions. The biogenic calcification, mainly including formations of foraminiferal shells and nannofossil, was active strongly. The calcium carbonate pump transported the dissolved inorganic carbon (as aqueous CO_2, HCO_3^-, and CO_3^{2-}) from surface to seafloor. The calcification mainly used carbon dissolved in seawater as HCO_3^-[13]. Two moles of HCO_3^- react with 1 mole of Ca^{2+} to precipitate 1 mole of $CaCO_3$, releasing the extra mole of carbon as CO_2 and reducing the CO_3^{2-} concentration in seawater (Fig. 1). Thus, biogenic calcification is a potential source of CO_2 to the atmosphere, rather than a carbon sink[10]. During the transitions of interglacials to glacials, the carbonate dissolution increased. To dissolve 1 mole of $CaCO_3$ requires 1 mole of CO_2, and produces 2 moles of HCO_3^-, increasing the CO_3^{2-} concentration in seawater. This $CaCO_3$ dissolution could occur during the settling of calcitic shells through the water column, within the species body's cavities, or in sediments on the seafloor[13]. During the last glacial Plateau region. Magnetic susceptibility correlates well period, for example, a study on the CO_3^{2-} concentration in seawater at the Ontong-Java Plateau in the western Pacific indicates that the CO_3^{2-} concentration at 3-km depth is 12 μmol/kg higher than that during the Holocene, and increases with the water depth[15]. For this case, the calcium carbonate pump transported CO_2 to the deep sea and becomes a sink of the atmospheric CO_2. Therefore, the calcium carbonate pump ultimately affects the CO_3^{2-} concentration and the pH in seawater. The CO_3^{2-} concentration is proportional to the pH and inversely proportional to the CO_2 concentration[10]. This is intuitively obvious: during interglacials, relatively lower CO_3^{2-} concentration and pH in seawater and relatively high atmospheric CO_2 concentration produce relatively higher global temperature because of the greenhouse effect; during glacials, relatively high CO_3^{2-} concentration in seawater made relatively lower atmospheric CO_2 concentration, and in turn relatively low global temperature.

(iv) Implications for global atmospheric pCO_2. According to the mechanism of calcium carbonate pump during the glacial cycles, changes in the CO_3^{2-} concentration must play a significant role in atmospheric pCO_2 variations[22]. The questions are "when" and "by how". The carbonate records from Site 1143 can address some of the two questions. The carbonate contents during the last three glacial-interglacial cycles at Site 1143 in the SCS are correlated to atmospheric pCO_2 and δD variations from the Vostok ice core in Antarctic[4] (Fig. 4), to determine effects of marine calcium carbonate pump on variations in the global atmospheric CO_2.

The atmospheric pCO_2 at Vostok started to increase at about 600±400 a after warming in the last three glacial-interglacial cycles, with an approximate 80%—100%. After the onset of glacials, the high atmospheric pCO_2 can last several thousands of years[4,40] (Fig. 4). During termination Ⅰ, the Vostok atmospheric pCO_2 and deep-sea

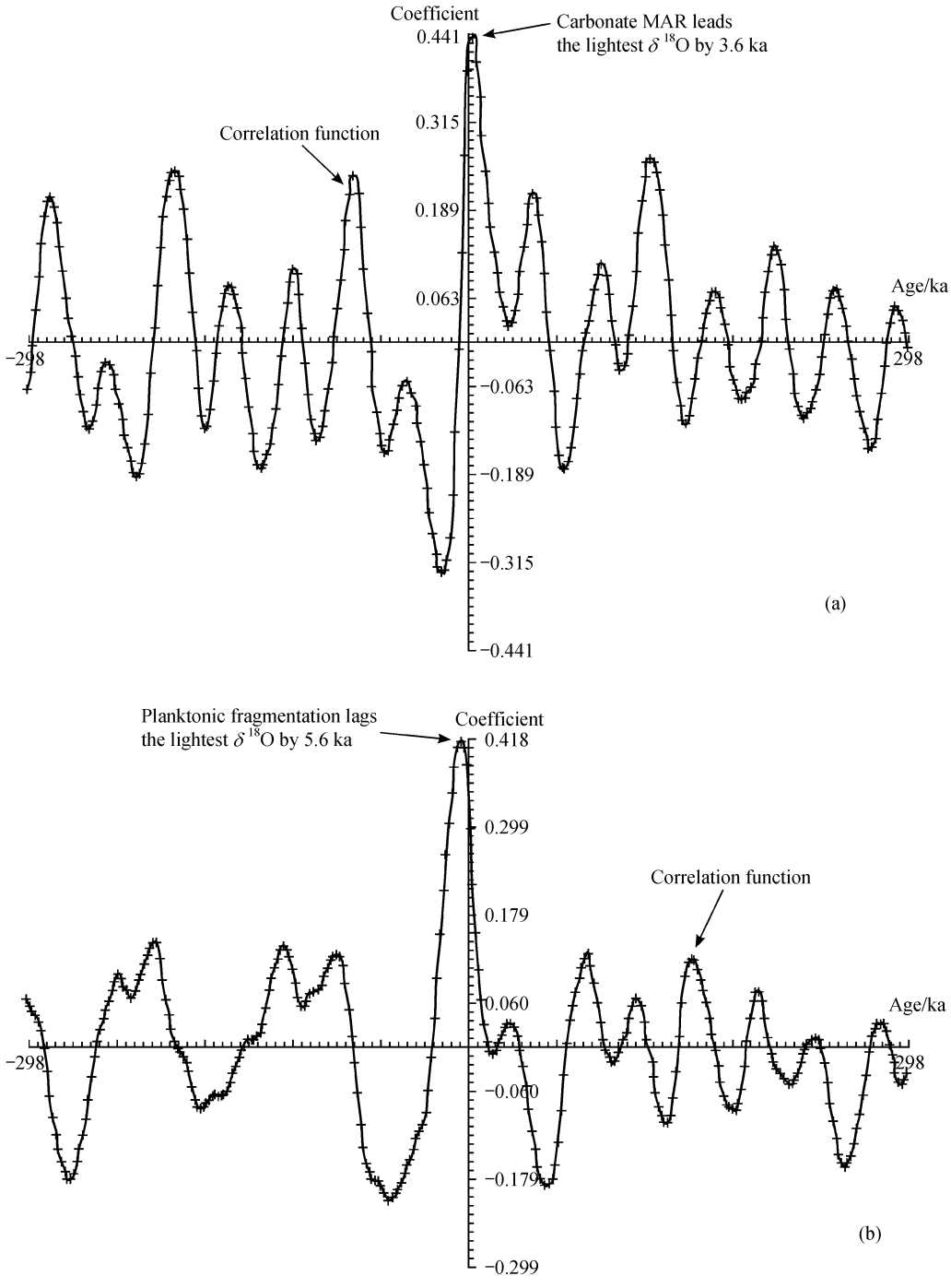

Fig. 3. Cross-correlation statistical analysis of benthic foraminiferal δ^{18}O with carbonate MAR and planktonic foraminiferal fragmentation. (a) benthic δ^{18}O with carbonate MAR; (b) benthic δ^{18}O with planktonic fragmentation. Software Arand[35] was used to perform the cross-correlation analysis, with 150 samples for each range and about 2 ka for the temporal resolution, and in turn for a maximum of 149 samples and a time difference of 298 ka. On the coordinate, a positive time refers to a lead and a negative one refers to a lag; a positive coefficient refers to positive correlation and a negative one refers to negative correlation.

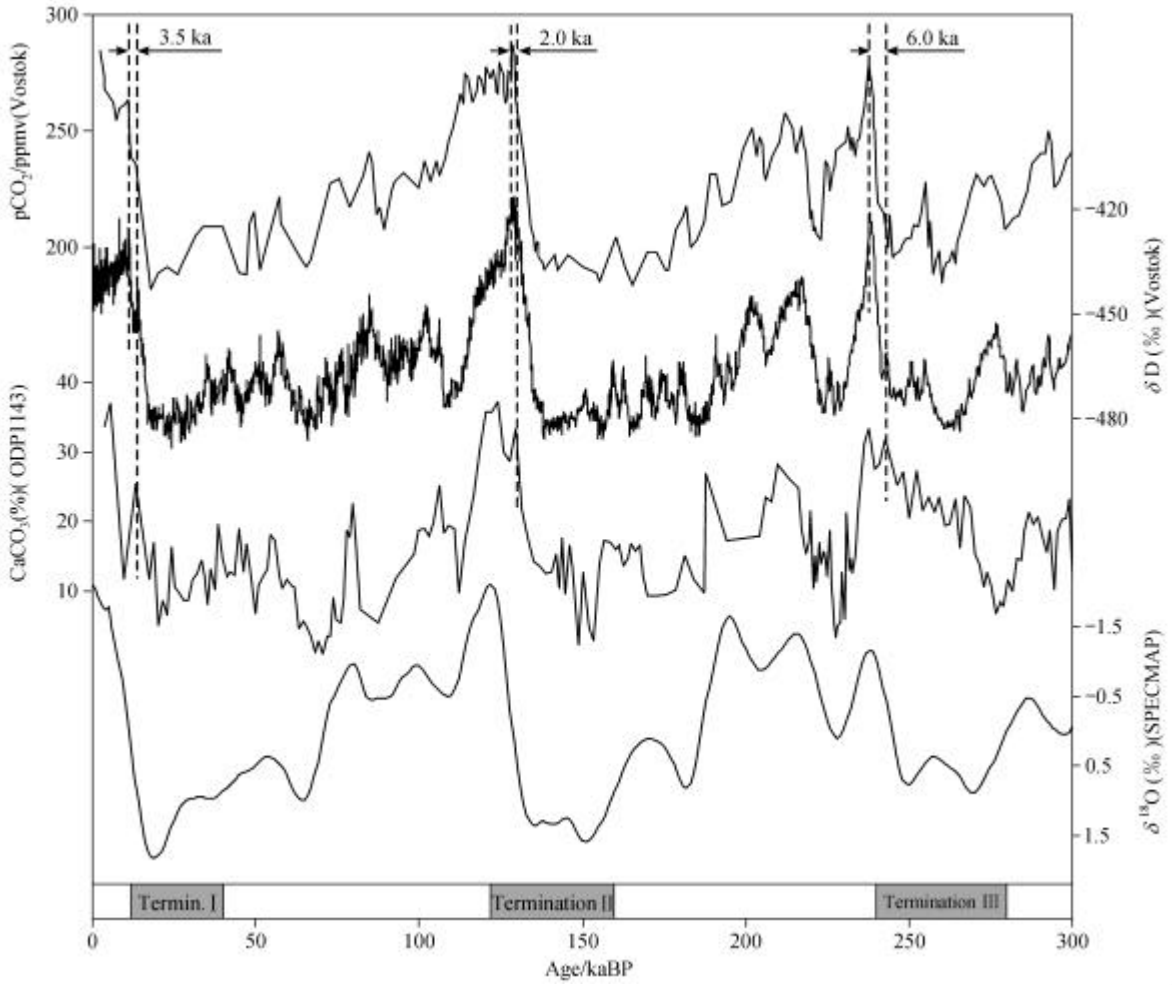

Fig. 4. Comparison of carbonate contents at ODP Site 1143 with pCO_2 and δD at Vostok ice core[4] in the last three glacial-interglacial cycles. δD is a proxy of the Antarctic temperature. Note that negative values referring cold weathers. The benthic foraminiferal $\delta^{18}O$ of SPECMAP[36] provides a history of global ice volume.

$CaCO_3$ increased synchronously at about 20 ka BP. The $CaCO_3$ reached its maximum at 14 ka BP, but the atmospheric pCO_2 reached its maximum at 10.5 ka BP, with a time difference of 3.5 ka. During termination Ⅱ, the Vostok atmospheric pCO_2 started to increase at 135 ka, a short later than that of the deep-sea $CaCO_3$. Similarly to the Holocene, the atmospheric pCO_2 reached its maximum at 128 ka BP, later than the $CaCO_3$ maximum by about 2.0 ka. During termination Ⅲ, two signals increased synchronously at 250 ka BP. the magnitude of variations in $CaCO_3$ is larger that that of fluctuations in atmospheric pCO_2. The atmospheric pCO_2 reached its maximum later than $CaCO_3$ by about 6.0 ka. The variations in the Vostok atmospheric pCO_2 generally lag those of deep-sea $CaCO_3$, implying a control of the marine calcium carbonate pump on parts of global changes in atmospheric CO_2. During the onset of terminations, the productivity of biogenic calcitic shells increased, and then the calcium carbonate pump released CO_2 to the atmosphere to improve the atmospheric pCO_2. After the formation of glacials, the carbonate dissolution increased, and the calcium carbonate pump transported the atmospheric CO_2 to the deep sea by the interaction between oceanic surface and atmosphere, to reduce the atmospheric pCO_2. Because of the buffer effect of CO_2[10], the high atmospheric pCO_2 usually lasted several thousands of years, rather than immediately deceasing after the onset of glacials. Previous works on the $CaCO_3$ dissolution cycles in the equatorial Pacific[14] suggested that the $CaCO_3$ dissolution events forced the onset of times of glaciation, implying a control of the calcium carbonate pump on the global atmospheric CO_2.

However, the marine calcium carbonate pump does not completely control all variations during glacial cycles. For example, the carbonate dissolution did not increase at

the transitions of isotope stages 7/6 and 27/26 at Site 1143; similarly, the carbonate MAR did not increase at the boundaries of isotope stages 20/19 and 26/25 (Fig. 2). Those imply complicated changes in the global atmospheric CO_2. The carbon on the Earth exists as inorganic and organic types and circulates between the atmosphere, hydrosphere, lithosphere, and biosphere. The atmospheric pCO_2 is a result of those circulations. Besides the control of the marine calcium carbonate pump on the atmospheric pCO_2, organic carbon pump[11,12] with a reversed process to the calcium carbonate pump, nutrient utilization in surface water at high latitudes[9], and variation in carbon reservoir at continental uplift regions contribute to the global climate changes. But, this paper presents a significant aspect of the global carbon cycle.

3 Conclusions

Carbonate contents, carbonate MAR, benthic foraminiferal $\delta^{18}O$, and planktonic foraminiferal fragmentation were analyzed with a high resolution over the past 2 Ma at ODP Site 1143 in the South China Sea to reveal the process of calcium carbonate pump during the Quaternary glacial cycles. The results indicate statistically that the highest carbonate accumulation rate leads the lightest $\delta^{18}O$ by about 3.6 ka at most of transitions from glacials to interglacials, implying that the higher productivity of biogenic calcitic shells produced relatively low CO_3^{2-} concentration and relatively high release of CO_2, and then relatively high atmospheric pCO_2 and global temperature. During most of glacial-interglacial transitions, the strongest carbonate dissolution lags the lightest $\delta^{18}O$ by about 5.6 ka, indicating that stronger carbonate dissolution made the calcium carbonate pump transporting atmospheric CO_2 to the deep sea, and produced relatively high CO_3^{2-} concentration and the pH in seawater, and in turn relatively low atmospheric pCO_2 and global temperature. The adjustable function of the calcium carbonate pump for the CO_3^{2-} concentration in seawater directly controls parts of global changes in atmospheric CO_2, and contributes to the global carbon cycle system.

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References

1. Hays, J. D., Imbrie, J., Shackleton, N. J., Variations in the Earth's orbit: pacemaker of the Ice Ages, Science, 1976, 194: 1121—1132.
2. Sigman, D. M., Boyle, E. A., Glacial/interglacial variations in atmospheric carbon dioxide, Nature, 2000, 407: 859—869.
3. Webb, R. S., Lehman, S. J., Rind, D. H. et al., Influence of ocean heat transport on the climate of the Last Glacial Maximum, Nature, 1997, 385: 695—699.
4. Petit, J. R., Jouzel, J., Raynaud, D. et al., Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica, Nature, 1999, 399: 429—436.
5. Adams, J. M., Faure, H., Faure-Denard, L. et al., Increases in terrestrial carbon storage from the Last Glacial Maximum to the present, Nature, 1990, 348: 711—714.
6. Guilderson, T. P., Fairbanks, R. G., Rubenstone, J. L., Tropical temperature variations since 20000 years ago: modulating interhemispheric climate change, Science, 1994, 263: 663—665.
7. Broecker, W., Peng, T.-H., The role of $CaCO_3$ compensation in the glacial to interglacial atmospheric CO_2 change, Glob. Biogeochem. Cycles, 1987, 1: 15—29.
8. McElroy, M. B., Marine geological controls on atmospheric CO_2 and climate, Nature, 1983, 302: 328—329.
9. Sarmiento, J. L., Toggweiler, J. R., A new model for the role of the oceans in determining atmospheric pCO_2, Nature, 1983, 308: 621—624.
10. Elderfield, H., Carbonate mysteries, Science, 2002, 296: 1618—1621.
11. Broecker, W. S., Ocean chemistry during glacial time, Geochim. Cosmochim. Acta, 1982, 46: 1689—1706.
12. Anderson, R. F., Chase, Z., Fleisher, M. Q. et al., The Southern Ocean's biological pump during the Last Glacial Maximum, Deep Sea Res. II, 2002, 49: 1909—1938.
13. Jansen, H., Modelling the marine carbonate pump and its implications on the atmospheric CO_2 concentration, Bremen: Universität Bremen (Dissertation), 2001, 1—128.
14. Broecker, W. S., Sanyal, A., Magnitude of the $CaCO_3$ dissolution events making the onset of times of glaciation, Paleoceanography, 1997, 12: 530—532.
15. Broecker, W. S., Clark, E., Glacial-to-Holocene redistribution of carbonate ion in the deep sea, Science, 2001, 294: 2152—2155.
16. Anderson, D. M., Archer, D., Glacial-interglacial stability of ocean pH inferred from foraminifer dissolution rates, Nature, 2002, 416: 70—73.
17. Keir, R. S., Berger, W. H., Atmospheric CO_2 content in the last 120,000 years: the phosphate-extraction model, J. Geophys. Res., 1983, 88: 6027—6038.
18. Peterson, L. C., Prell, W. L., Carbonate preservation and rates of climatic change: an 800 kyr record from the Indian Ocean (eds. Sundquist, E. T., Broecker, W. S.), The Carbon Cycle and Atmospheric CO_2: Natural Variations Archean to Present, Washington, D. C.: AGU, Geophys. Monogr. 32, 1985, 251—269.
19. Wu, G., Yasuda, M. K., Berger, W. H., Late Pleistocene carbonate

stratigraphy on Ontong-Java Plateau in the western equatorial Pacific, Mar. Geol., 1991, 99: 135—150.
20. Le, J., Shackleton, N. J., Carbonate dissolution fluctuations in the western equatorial Pacific during the Late Quaternary, Paleoceanography, 1992, 7: 21—42.
21. Curry, W. B., Lohmann, G. P., Late Quaternary carbonate sedimentation at the Sierra Leone Rise (eastern equatorial Atlantic Ocean), Mar. Geol., 1986, 70: 223—250.
22. Hodell, D. A., Charles, C. D., Sierro, F. J., Late Pleistocene evolution of the ocean's carbonate system, Earth Planet. Sci. Lett., 2001, 192: 109—124.
23. Sanyal, A., Hemming, N. G., Hanson, G. N. et al., Evidence for a higher pH in the glacial ocean from boron isotopes in foraminifera, Nature, 1995, 373: 234—236.
24. Wang, H., Jain, Z., Carbonate dilution cycles in the late Quaternary South China Sea (eds. Ye, Z., Wang, P.), Contributions to Late Quaternary Paleoceanography of the South China Sea (in Chinese with English abstract), Qingdao: Qingdao Ocean Univ. Press, 1992, 283—294.
25. Wang, P., Prell, W. L., Blum, P. et al., Proceedings of the ODP, Initial Reports 184, College Station: Ocean Drilling Program, Texas A&M University, 2000, 1—103 [CD-ROM].
26. Rottmann, M. L., Dissolution of planktonic foraminifera and pteropods in South China Sea sediments, J. Foraminiferal Res., 1979, 9: 41—49.
27. Miao, Q. R., Thunell, C., Anderson, D. M., Glacial-Holocene carbonate dissolution and sea surface temperatures in the South China and Sulu seas, Paleoceanography, 1994, 9: 269—290.
28. Hanebuth, T., Stattegger, K., Grootes, P. M., Rapid flooding of the Sunda Shelf: A late-glacial sea-level record, Science, 2000, 288: 1033—1035.
29. Thunell, R. C., Miao, Q., Calvert, S. E. et al., Glacial-Holocene biogenic sedimentation patterns in the South China Sea: Productivity variations and surface water pCO_2, Paleoceanography, 1992, 7: 143—162.
30. Wang, P., Tian, J., Cheng, X., Transition of Quaternary glacial cyclicity in deep-sea records at Nansha, the South China Sea, Science in China, Ser. D, 2001, 44(10): 926—933.
31. Shackleton, N. J., Berger, A., Peltier, W. R., An alternative astronomical calibration of the lower Pleistocene timescale based on ODP Site 677, Transactions of the Royal Society of Edinburgh: Earth Sciences, 1990, 81: 251—261.
32. Tian, J., Wang, P., Cheng, X. et al., Astronomically tuned Plio-Pleistocene benthic $\delta^{18}O$ record from South China Sea and Atlantic-Pacific comparison, Earth Planet. Sci. Lett., 2002, 203: 1015—1029.
33. Jones, A., Kaiteris, P., A vacuum gasometic technique for rapid and precise analysis of calcium carbonate in sediments and soils, J. Sediment. Petrol., 1983, 53: 655—660.
34. Howard, W. R., Prell, W. L., Late Quaternary $CaCO_3$ production and preservation in the Southern Ocean: Implications for oceanic and atmospheric carbon cycling, Paleoceanography, 1994, 9: 453—482.
35. Howell, P., ARAND time series and spectral analysis package for the Macintosh, Brown University, IGBP PAGES/World Data Center for Paleoclimatology Data Contribution Series #2001-044, Boulder, Colorado, USA: NOAA/NGDC Paleoclimatology Program, 2001.
36. Imbrie, J., Hays, J. D., Martinson, D. G. et al., The ordital theory of Pleistocene climate: A support from a revised chronology of the marine $\delta^{18}O$ record (eds. Berger, A., Imbrie, J.), Milankovitch and Climate, Mass: Hingham, 1984, 269—305.
37. Ruddman, W. F., Pleistocene sedimentation in the equatorial Atlantic: Stratigraphy and faunal paleoclimatology, Bull. Geol. Soc. Am., 1971, 82: 283—302.
38. Wang, P., Min, Q., Bian, Y. et al., Planktonic foraminifera in the continental slope of the northern South China Sea during the last 130,000 years and their paleoceanographic implications, Acta Geol. Sin. (in Chinese and English abstract), 1986, 60: 215—225.
39. Wang, P., Wang, L., Bian, Y. et al., Late Quaternary paleoceanography of the South China Sea: surface circulation and carbonate cycles, Mar. Geol., 1995, 127: 145—165.
40. Fischer, H., Wahlen, M., Smith, J. et al., Ice cope records of atmospheric CO_2 around the last three glacial terminations, Science, 1999, 283: 1712—1714.

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