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INTERANNUAL ^{14}C VARIATIONS DURING 1977–1998 RECORDED IN CORAL FROM DAYA BAY, SOUTH CHINA SEA

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ABSTRACT. Twenty-two annually banded samples of coral from 1977 to 1998 were collected from Daya Bay, South China Sea, and bomb ^{14}C concentrations were determined. The interannual variation of coral $\Delta^{14}C$ is controlled mainly by oceanic factors. In ENSO years, the coastwise upwelling current of the South China Sea has been intensified; hence, the coral $\Delta^{14}C$ displays its minimum value. The interannual variation curve of $\Delta^{14}C$ in coral bears a relationship with the Southern Oscillation Index (SOI) curves: the correlation coefficient between $\Delta^{14}C$ and $(SOI)_w$ is 0.43 and the correlation coefficient between $\Delta^{14}C$ and $(SOI)_y$ is 0.27. The coral $\Delta^{14}C$ has no remarkable response to the variation of solar radiation energy. In the past 20 yr or so, the general situation and oceanic thermal structure of the South China Sea are still stable even though interannual variations in atmosphere-sea interaction and upwelling current driven by the tropical energy have occurred.

INTRODUCTION

Radioactive isotope tracers such as radiocarbon, ^{3}H, ^{222}Rn, and ^{226}Ra are widely applied in oceanological research simply because these radioactive isotopes can be indicative of some extremely slow processes occurring in seawater, which may include offshore vertical mixing (and its rate), deep-water mixing (and its rate), thermocline vertical mixing (and its rate), upwelling current, oceanic transverse mixing, and so on (Broecker 1974). The conventional oceanological methods are usually useless in the study of these extremely slow processes. Natural ^{14}C and bomb ^{14}C are also the most ideal isotope tracers when studying the interaction processes and their exchange rates between the atmosphere and the oceans (Nydal 2000; Levin et al. 2000).

It is usually considered that carbon isotopes in coral skeletons have attained equilibrium with the inorganic carbon isotopes in ambient seawater (Druffel 1982). Therefore, the ^{14}C variation in annual bands of coral can be used to reveal the interannual variation of ^{14}C in the dissolved inorganic carbon in surface seawater during the growing period of coral. The $\Delta^{14}C$ record of tropical coral from the Atlantic Ocean, the Pacific Ocean, and the Indian Ocean can undoubtedly yield important information about ocean current circulation. Based on the $\Delta^{14}C$ record of coral growing during the 1960s to 1970s from the Sargasso Sea area in the Atlantic Ocean, Druffel et al. (1983, 1986) pointed out that the renewal rate of water mass in this area decreased gradually. Druffel et al. (1989, 1993) also contended, based on the seasonal and annual variations of bomb ^{14}C in coral from middle Pacific Ocean, that the "transequatorial transport of surface currents" characterized by seasonal variations is the dominant factor that controls bomb ^{14}C variation. Research by Toggweiler et al. (1991) on coral ^{14}C in the temperate and tropic zones of the Pacific Ocean before nuclear weapon testing demonstrates that the thermocline seawater in the South Pacific Ocean is characterized by a low $\Delta^{14}C$ value (just like the Subantarctic mode water mass, the 13 °C water mass in the Equator, and the Peruvian upwelling current). This is simply attributed to the fact that the Subantarctic mode water mass with a low ^{14}C value is injected into the thermocline from the northern margin of the Antarctic circumpolar current (Guilderson and Schrag 1998). Recently, Guilderson et al. (1998) have conducted research on ^{14}C of coral from the Galapagos Islands in the East Pacific Ocean, indicating that the $\Delta^{14}C$ and the surface seawater temperature (SST) tend to increase in the seasons with upwelling

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(July to September) since 1976. The synchronous variation of ^{14}C and SST implies that a change in thermal structure has taken place in a vertical direction in the tropical East Pacific Ocean after 1976. This change could be the main factor responsible for the increased frequency and intensity of the occurrence of ENSO (Guilderson et al. 1998).

This study is mainly focused on *Platygyra* collected from Daya Bay in the South China Sea. The interannual ^{14}C variations in coal samples collected annually are discussed to reveal the characteristics of atmosphere-sea gas exchange and the rules governing the evolution of related climatic events in this sea area.

SAMPLES, METHODS, AND RESULTS

The coral samples examined in this study were collected from Daya Bay in the South China Sea. The sampling sites are about 1.5 km from the thermal effluent outlet of the Daya Bay Nuclear Power Station, and about 10–15 m from the sandy beach (coast). Figure 1 is a map showing the geographical position of Daya Bay and the sampling location. The samples were *Platygyra* sp. collected in October 1998 (Yu et al. 2002). One of our co-authors, Kefu Yu, provided a sectioned slice of the original coral measured at 1 cm thickness, together with its X-radiograph film chart. Annual bands were scored according to the growth lines shown on the sectioned coral sample, and a total of 22 specimens of annual bands from 1977 to 1998 were taken for ^{14}C measurement. All the specimens are composed of spotlessly white crystallized $CaCO_3$-aragonite.

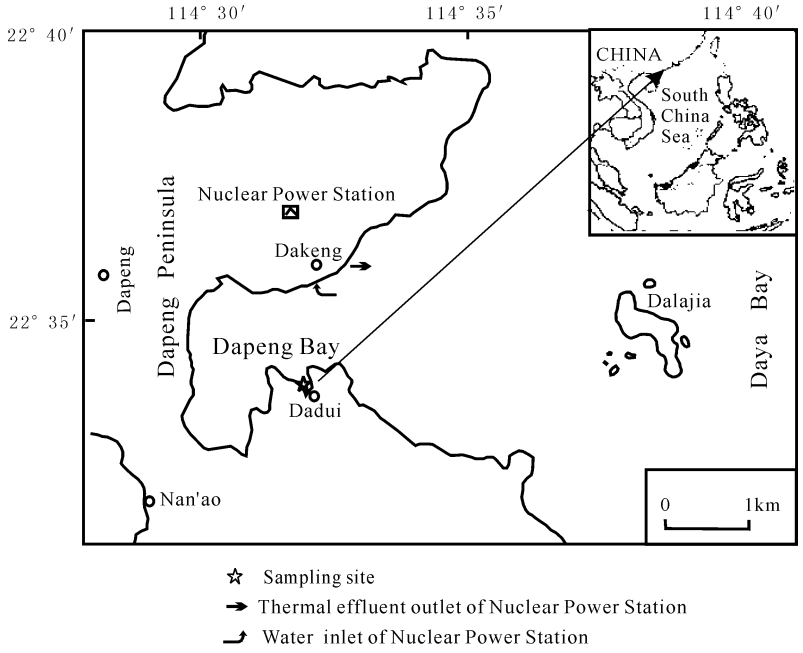

Figure 1 Map showing the geographical position of Daya Bay in the South China Sea

From each annual band, specimens of 5–10 g were taken out, rinsed with deionized water in a supersonic water bath, then acidified with 10% HCl in a glass reactor linked with a vacuum system to derive CO_2. CO_2 gas was repeatedly purified in a series of "liquid nitrogen-dry ice + acetone-liquid nitrogen" traps in the vacuum system, and was finally used to synthesize Li_2C_2 in a stainless steel

reactor under high temperature (900 °C) and vacuum conditions. In succession, Li_2C_2 was hydrolyzed into acetylene (C_2H_2), which was then used to synthesize benzene (C_6H_6) with catalysts. ^{14}C determination for all samples was accomplished on a 1220 Quantulus liquid scintillation counter with extremely low background at the Guangzhou Institute of Geochemistry, the Chinese Academy of Sciences. The results are listed in Table 1, together with the average thickness of the annual growth layer of coral samples, as well as the 1977–1997 atmospheric temperature and 1977–1998 precipitation recorded by the local meteorological observation station (Pan and Wang 1998). In order to conduct a comparative study, the atmospheric ^{14}C data, as recorded in North European tree rings in the Northern Hemisphere on a corresponding timescale (Nydal 2000), are also listed in Table 1. It can be seen from Table 1 that the $\Delta^{14}C$ values of annual bands of the coral samples from 1977–1998 are all greater than zero, which clearly suggests that the contribution of bomb ^{14}C could not be ruled out.

Table 1 ^{14}C measurement results for coral from Daya Bay, South China Sea.

Field code	Lab code	Year	Average thickness of annual growth layer (cm a^{-1})	Atmospheric temperature (°C)	Precipitation (mm)	Atmospheric $\Delta^{14}C$ (‰)	Coral $\Delta^{14}C$ (‰)
DYW-08-1	GC-00081	1977	1.69	22.1	1458.5	335	240
DYW-08-2	GC-00082	1978	1.67	21.8	1930.2	335	230
DYW-08-3	GC-00083	1979	1.56	21.8	2530.0	299	120
DYW-08-4	GC-00084	1980	1.64	22.0	1736.4	271	220
DYW-08-5	GC-00085	1981	1.71	21.9	1986.7	260	190
DYW-08-6	GC-00086	1982	1.69	21.9	1761.3	244	200
DYW-08-7	GC-00087	1983	1.25	21.7	2583.7	223	100
DYW-08-8	GC-00088	1984	1.34	21.4	1438.6	209	160
DYW-08-9	GC-00089	1985	1.54	21.8	1762.2	200	240
DYW-08-10	GC-00090	1986	1.41	21.9	1961.2	186	250
DYW-08-11	GC-00091	1987	1.38	22.7	2038.2	183	160
DYW-08-12	GC-00092	1988	1.33	21.8	1609.7	169	190
DYW-08-13	GC-00093	1989	0.93	22.3	1704.8	159	190
DYW-08-14	GC-00094	1990	0.96	22.5	1469.3	149	200
DYW-08-15	GC-00095	1991	1.29	22.8	1728.3	138	230
DYW-08-16	GC-00096	1992	1.05	22.0	1888.8	134	100
DYW-08-17	GC-00097	1993	1.06	22.3	1843.5	126	140
DYW-08-18	GC-00098	1994	1.03	22.0	2075.5	120	220
DYW-08-19	GC-00099	1995	0.91	21.4	1656.0	112	200
DYW-08-20	GC-00100	1996	0.99	21.8	1716.9	104	250
DYW-08-21	GC-00101	1997	1.33	21.8	2474.6	—	190
DYW-08-22	GC-00102	1998	1.37	—	2081.0	—	230

DISCUSSION

The Response of Coral $\Delta^{14}C$ to Atmospheric ^{14}C Annual Variation

Generally, ^{14}C finds its way into surface seawater with atmospheric CO_2 through the atmosphere-sea gas exchange mechanism. The dissolution process of CO_2 in seawater is described as follows:

$$CO_2 + H_2O <=> H_2CO_3$$

$$H_2CO_3 <=> HCO_3^- + H^+$$

$$HCO_3^{-1} <=> CO_3^{2-} + H^+$$

As viewed from ^{14}C tracing of the atmosphere-sea gas exchange process, one can see that in seawater there are a variety of forms of carbon, such as carbonate, bicarbonate, and dissolved CO_2; their summation is referred to as the total carbon dioxide (ΣCO_2). The concentrations of various carbon components in seawater can be calculated in terms of its temperature, salinity, pH value, total alkalinity, etc. (Broecker 1974). The total CO_2 in seawater at Daya Bay is comprised mainly of HCO_3^{-1} (about 89%), and subordinately of CO_3^{-2} (about 11%), and dissolved CO_2 (about 0.5%) (Han 1998). Based on the gas exchange of CO_2 between air and sea, as well as chemical reactions in the seawater, the coral ^{14}C has attained equilibrium with the dissolved inorganic carbon (DIC) in ambient seawater, i.e., $\Delta^{14}C_{coral} = \Delta^{14}C_{DIC}$ (Druffel 1982).

Figure 2 illustrates the interannual variation curve of $\Delta^{14}C$ from 1977–1998 for the Daya Bay coral samples, together with the interannual variation curve of atmospheric $\Delta^{14}C$ from 1977–1996, as reflected by the north European tree rings. The small block diagram in the upper right presents the variation curve of atmospheric $\Delta^{14}C$ on an even longer timescale, i.e., since the early 1950s, as reflected by the north European tree rings. It can be seen from the small block diagram that due to the atmospheric nuclear weapon testing, the atmospheric ^{14}C concentrations had rapidly increased year by year in the period from the early 1950s to the early 1960s, and reached the maximum of 900‰ in 1963 (Nydal 2000). After the treaty banning atmospheric nuclear weapon testing went into effect, the atmospheric $\Delta^{14}C$ decreased slowly, and $^{14}CO_2$ found its way into the ocean through atmosphere-sea gas exchange and oceanic vertical mixing. Figure 2 is actually a magnification of the dashed block inside the small block diagram, and it can be seen that the 2 curves are completely different: the tree-ring ^{14}C displays noticeable exponential attenuation, i.e., 80% decrease in about 20 yr, while the coral ^{14}C fluctuates in large amplitude around the mean value of 200‰. Since coral ^{14}C attained equilibrium with dissolved inorganic carbon ^{14}C in its ambient seawater, and the $^{14}CO_2$ that was input into the ocean is directly proportional to the $^{14}CO_2$ concentration gradient between the atmosphere and surface seawater, the variation of ^{14}C concentration in the coral annual layers with time can be expressed as:

$$\frac{^{14}C_s}{dt} = \frac{D}{ZM}(^{14}C_S - {}^{14}C_A),$$

where $^{14}C_S$ is the ^{14}C concentration in surface seawater, $^{14}C_A$ is the ^{14}C concentration of atmospheric CO_2, Z is the diffusion thickness and M is the depth of seawater where coral grows.

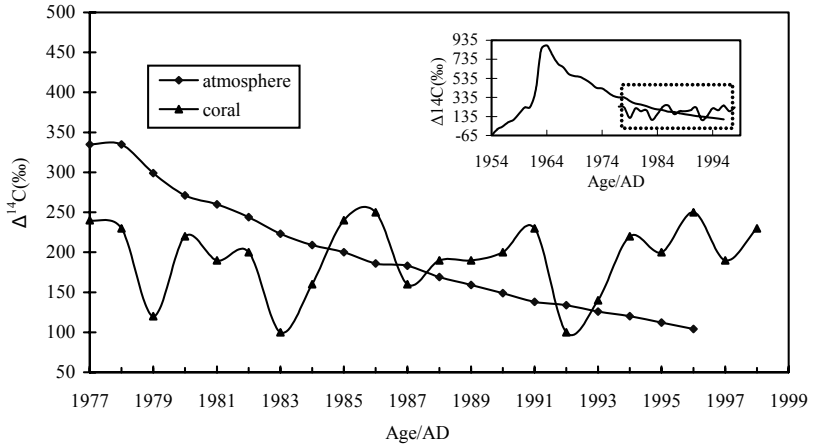

Figure 2 $\Delta^{14}C$ interannual variations of coral samples from Daya Bay and those of the atmosphere

The $\Delta^{14}C$ of annual bands of coral from Daya Bay during 1977–1998 varies from 100‰ to 250‰, which is larger than the $\Delta^{14}C$ value range of 70‰–110‰ in coral from the northwest Pacific for the same period (Morimoto et al. 2004). Perhaps because the sample localities are distributed near the coast, the ^{14}C concentrations of surface seawater ($^{14}C_S$), and hence the coral ^{14}C concentrations, could be influenced by terrestrial freshwater.

Response of Coral $\Delta^{14}C$ to ENSO

It is well known that ENSO—an abnormal phenomenon of climatic change resulting from a complex interaction between the tropical Pacific Ocean and the atmosphere—is the strongest signal of interannual climatic change so far discovered by meteorologists. During an ENSO event, the SST of the western Pacific will be at least 0.5 °C higher than the average value and the duration will be half a year or even longer (McCreary 1983; Huang 2001). The so-called SOI (Southern Oscillation Index) refers to the sea level atmospheric pressure difference between the Darwin and Tahiti areas, which is used as a primary measure of the state of the ENSO system. The available studies have shown that there is a close relationship between SOI and ENSO (Troup 1965; Rasmusson and Wallace 1983). The interannual variation curve of $\Delta^{14}C$ in coral from Daya Bay (Figure 3) can be compared with the SOI curves. $(SOI)_y$ and $(SOI)_w$ represent the monthly average for the entire year and in winter, respectively. The 3 curves display a correlated tendency of variation: the correlation coefficient between $\Delta^{14}C$ and $(SOI)_w$ is 0.43 and the correlation coefficient between $\Delta^{14}C$ and $(SOI)_y$ is 0.27. Ropelewski (1992) points out that during the ENSO years, the precipitation is relatively low and the atmospheric temperature is slightly higher during winter in the South China Sea region, presenting warm-dry climate environmental characteristics. Studies of coral samples taken from the subtropical northwestern Pacific have shown that $\Delta^{14}C$ variation reaches the maximum annual extent in winter season, higher than the average by 20% (Morimoto et al. 2004). The above studies and this work have revealed that there is a better correlation between $\Delta^{14}C$ and $(SOI)_w$. In light of the data on precipitation and atmospheric temperature listed in Table 1, a statistical treatment was carried out. Obviously, from the regression analysis in the 20-yr period from 1977 to 1996, the temperature tends to increase, while precipitation tends to decrease. As a matter of fact, comparison of the average values in the former 10 yr (1977–1986) with those in the latter 10 yr (1987–1996) provides evidence that the atmospheric temperature has risen by 0.40 °C and the precipitation has decreased by 140 mm, showing a tendency of warm-dry climatic change.

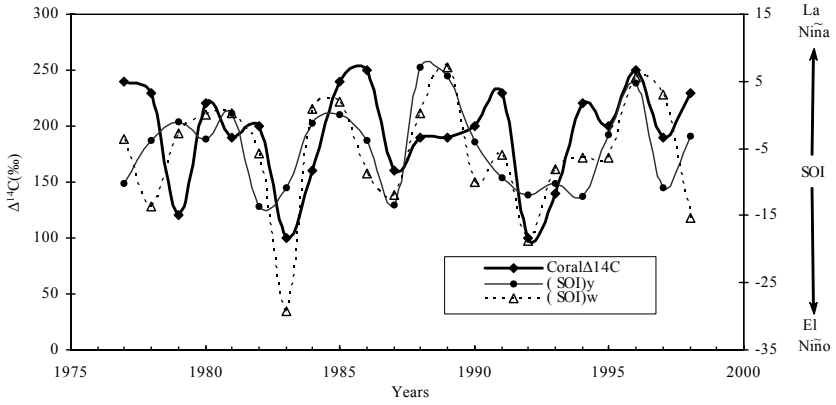

Figure 3 Interannual $\Delta^{14}C$ variations in the coral from Daya Bay and the variation trends of SOI

It is worth noting that the years during which great decreases in $\Delta^{14}C$ occur (for example, 1978–1979, 1982–1983, 1986–1987, 1991–1992, and 1996–1997) correspond precisely to or are within 1 yr of ENSO events. The southwestern monsoon is very prevalent in summer along the coast in eastern Guangdong, and the gale usually results in the offshore movement of surface seawater, causing the deep-layer seawater to upwell for replenishment and forming an upwelling current along the coast. The upwelling current is characterized by low temperature, high salinity, and low ^{14}C radioactivity, which is reflected in the coral record. On the contrary, based on coral $\Delta^{14}C$ variation, one can see that the upwelling current in the South China Sea intensified during ENSO years.

Response of Coral $\Delta^{14}C$ to Solar Radiation

The South China Sea, which is located in a low-latitude area, is a tropical sea and is subject to plenty of solar radiation energy. There is an obvious latitudinal difference for the solar radiation energy to be received by the earth's surface (including the land surface and the ocean surface). Driven by the tropical energy, the water vapor over the South China Sea will be conveyed toward the continent; in fact, the water vapor brought about by summer monsoon in China mainly comes from the South China Sea. Willson (1997) pointed out that the year with the minimum total radiation for the 21st solar activity cycle is 1986/1987, while that for the 22nd solar activity cycle is 1996/1997. Between these 2 yr featuring minimum total radiation, the total solar radiation increased by 0.036%. Table 1 shows atmospheric temperature data recorded in the past 20 yr from 1976 to 1997 by a local meteorological observation station (Pan et al. 1998). It can be estimated from Table 1 that in the 2 decades from 1977 to 1986 and from 1987 to 1996, the 10-yr average atmospheric temperature increased by 0.40 °C from the first decade to the second decade, corresponding to the increasing trend of total solar radiation mentioned above. It also can be seen from the atmospheric $\Delta^{14}C$ variation curve as shown in Table 1 and Figure 2 that in the 2 decades from 1977 to 1986 and from 1987 to 1996, the average atmospheric $\Delta^{14}C$ decreased from 256.2‰ for the first decade to 139.4‰ for the second decade. There are 2 obvious causes for the $\Delta^{14}C$ decrease: 1) the ever increasing consumption of fossil fuels results in further dilution of the atmospheric ^{14}C concentrations by ^{14}C-free CO_2; 2) the atmospheric nuclear weapon testing-derived ^{14}C continues to be absorbed by the vast ocean. Figure 2 shows that for coral from Daya Bay, the average $\Delta^{14}C$ value is 195.0‰ in the first decade and 207‰ in the second decade, respectively, i.e., almost no obvious change has ever taken place in the 10-yr average value of $\Delta^{14}C$, which demonstrates that the $\Delta^{14}C$ value of coral does not respond noticeably to the variation of solar radiation energy. It is apparent that, although apparent interannual variations occur in atmosphere-sea interaction and upwelling activity as driven by the tropical energy, no big fluctuation has ever occurred for the $\Delta^{14}C$ of South China Sea water during the 2 decades, from which we can conclude that the general situation and the oceanic thermal structure of the South China Sea are relatively stable. Nevertheless, whether various changes observed in solar radiation equilibrium in the 2 recent 10-yr time periods were caused by natural variability or by those factors that are well known to be closely associated with global change needs further study (Wielicki et al. 2002).

CONCLUSIONS

From the study of interannual variation of bomb ^{14}C in coral *Platygyra* from Daya Bay, some preliminary conclusions can be drawn as follows:

1. The coral $\Delta^{14}C$ interannual variation is controlled mainly by a series of oceanic factors, such as atmosphere-sea exchange, upwelling, etc. In the years of ENSO, upwelling in the South China Sea is intensified and the coral absorbs the seawater with low ^{14}C radioactivity, which has been brought upward to surface layers by the upwelling current, leading to a decrease in coral $\Delta^{14}C$.

2. The interannual variation curve of $\Delta^{14}C$ in coral from Daya Bay bears a relationship with SOI curves: the correlation coefficient between $\Delta^{14}C$ and $(SOI)_w$ is 0.43 and the correlation coefficient between $\Delta^{14}C$ and $(SOI)_y$ is 0.27.
3. Coral $\Delta^{14}C$ does not show any apparent response to the solar radiation energy in the past 20 yr from 1977 to 1997. Although interannual variations occur in atmosphere-sea interaction and upwelling activity driven by the tropical energy, the general situation and the oceanic thermal structure of the South China Sea still remain unchanged.

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