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SEASONAL ^{14}C AND SR/CA RECORDS OF A MODERN CORAL AROUND DAYA BAY NUCLEAR POWER PLANTS

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ABSTRACT. Due to an increasing number of nuclear reactors in operation, the radiocarbon (^{14}C) released from nuclear power plants (NPPs) has become an important anthropogenic source of ^{14}C. The examination of seasonal $\Delta^{14}C$ and monthly Sr/Ca, Mg/Ca variations in a coral in Daya Bay (China) shows that NPPs located there have an impact on the $\Delta^{14}C$ level and sea surface temperature (SST). The Mg/Ca variation was in good correlation with the Pacific Decadal Oscillation (PDO) before the operation of Ling'ao NPP in 2002, but this correlation became weak due to an abnormally higher SST after 2002. As illustrated by the $\Delta^{14}C$ variation in the coral, there were two relative increases of $\Delta^{14}C$ values in 1994 and 2002 when Daya Bay NPP and Ling'ao NPP began operations, respectively. The ^{14}C released from NPPs, instead of oceanic circulation, is probably the primary factor on the $\Delta^{14}C$ variation in Daya Bay during the NPPs' operation. The relative increase in $\Delta^{14}C$ value was ~80‰, which equals to ~18 Bq/kgC in specific activity. The seasonal variability in $\Delta^{14}C$ value usually peaked in summer, the real reason of which was unknown. This study sheds light on how the NPPs influence the ^{14}C content and SST in surrounding marine environment.

KEYWORDS: modern coral, radiocarbon, nuclear power plants, upwelling, Daya Bay, Sr/Ca, Mg/Ca.

INTRODUCTION

Radiocarbon (^{14}C) is not only an excellent dating tool, but also a great tracer in atmospheric and oceanic circulations. It is produced naturally by the reaction of cosmic-ray neutron and ^{14}N (Equation 1) in the troposphere and stratosphere. The ^{14}C atom is quickly oxidized into $^{14}CO_2$ and diffuses into the biosphere. The concentration of ^{14}C in air closely correlates to the cosmic ray flux and heliospheric modulation before the industrial revolution (Stuiver et al. 1991; Usoskin et al. 2004). Modern human activities have had significant effects on the ^{14}C concentration since the industrial revolution. Extensive use of fossil fuel significantly lowers the atmospheric $^{14}CO_2$ value by contributing ^{14}C-free CO_2 to the atmosphere, which is called the Suess Effect (Suess 1955; Guilderson et al. 2005; Pazdur et al. 2007). Another anthropogenic influence is the nuclear weapon tests from the 1950s to 1960s, which increased the atmospheric $^{14}CO_2$ concentration by ~980‰ in $\Delta^{14}C$ (Nydal and Lovseth 1983; Levin and Hesshaimer 2000; Hua and Barbetti 2013). After the Nuclear Test Ban Treaty was signed in 1963, the $^{14}CO_2$ concentration has been decreasing due to the exchange between the atmosphere and other carbon reservoirs (Levin and Kromer 2004).

Nuclear power plants (NPPs) can produce ^{14}C by thermal neutrons and/or fast neutrons reactions (Equations 1–5), and impact the ^{14}C concentration in surrounding environments (Davis 1977; Yim and Caron 2006):

$$n + {}^{14}N \rightarrow {}^{14}C + p \quad (1)$$

$$n + {}^{13}C \rightarrow {}^{14}C + \gamma \quad (2)$$

$$n + {}^{17}O \rightarrow {}^{14}C + {}^{4}He \quad (3)$$

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$$n + {}^{15}N \rightarrow {}^{14}C + {}^{2}D \quad (4)$$

$$n + {}^{16}O \rightarrow {}^{14}C + {}^{3}He \quad (5)$$

There are six major types of reactors: pressurized water reactor (PWR), boiling water reactor (BWR), pressurized heavy water reactor (PHWR), gas-cooled reactor (GCR), light water graphite-moderated reactor (LWGR), and fast breeder reactor (FBR) (Pieroni et al. 2008). Production of ^{14}C from NPPs differs depending on the types of reactors. Equations (3) and (5) usually occur when water is used as coolant (e.g. light water reactors PWR and BWR) or oxides exist in the fuel and moderators (Davis 1977; Molnar et al. 2002). As a result, there is likely more ^{14}C in the form of hydrocarbon in the liquid effluent from light water reactors than others. Equation (2) is only significant in high-temperature GCR. Equations (1) and (4) will happen in reactors with N_2 in the fuel, moderator or coolant (e.g. HWR with N_2 in the CO_2 coolant) (Povinec et al. 2009).The HWR, therefore, could have more $^{14}CO_2$ in gaseous effluent. Practically, Equations (4) and (5) have too low cross-sections to really occur (Davis 1977; Chudy and Povinec 1982).

Two NPPs were established in Daya Bay during the last two decades: one is Daya Bay NPP (DNPP, 2 reactors), which is also the first commercial NPP in Mainland China; the other is the Ling'ao NPP (LNPP, 4 reactors). The two NPPs both use PWRs based on the Framatone ANP French three-cooling-loop design (http://china.org.cn/environment/2011-03/29/content_22248031.htm). Therefore, the possible productions of ^{14}C in PWRs are Equations (1), (3) and (5). The airborne ^{14}C released from PWR are mainly hydrocarbons (70–95%) and partly CO and CO_2 (5–25%) (Uchrin et al. 1998; Svetlik et al. 2006). The ^{14}C in the liquid releases from PWR are carbonates and various organic compounds, but their relative quantities being currently unknown (IAEA 2004). The 6 reactors in Daya Bay provide an annual electrical output of 5802 MWe to the surrounding areas, including Hong Kong. Table 1 lists the information about the reactors in DNPPs and LNPPs. Before 2011, only noble gases, iodine and particles (half-life $\geq$ 8d) in gas effluents, and tritium and other nuclides in liquid effluents were required to be monitored in the Regulation for Environmental Radiation Protection of NPPs in mainland China (GB6249 1986). Radiocarbon and tritium in gas effluents and ^{14}C in liquid effluents have been added to the routine control after 2011 (GB6249 2011).

Table 1 Reactor types, operation dates, and capacities of DNPPs, LNPPs, and QNPPs (Chen et al. 2010; Wang et al. 2012; Yang et al. 2012).

Reactor (type)	Operation date	Capacity (MW_e)
DNPP1 (PWR)	08/31/1993	984
DNPP2 (PWR)	02/07/1994	984
LNPPI1 (PWR)	02/26/2002	984
LNPPI2 (PWR)	09/14/2002	984
LNPPII1 (PWR)	09/15/2010	1086
LNPPII2 (PWR)	08/07/2011	1086
QNPPI (PWR)	12/15/1991	310
QNPPII 1 (PWR)	02/06/2002	650
QNPPII 2 (PWR)	03/11/2004	650
QNPPIII 1 (HWR)	11/19/2002	720
QNPPIII 2 (HWR)	06/12/2003	720

Therefore, the ^{14}C record in effluents from NPPs in Daya Bay is only available from 2011 onward.

Previous studies of ^{14}C released from NPPs mainly focused on the airborne ^{14}C, coolants, and tree rings (McCartney et al. 1986; Levin et al. 1988; Hertelendi et al. 1989; Loosli and Oeschger 1989; Uchrin et al. 1992; Milton et al. 1995; Stenstrom et al. 1998; Roussel-Debet et al. 2006; Povinec et al. 2009; Vaitkeviciene et al. 2013). Unlike tree rings at high latitudes, the tree rings in Daya Bay are not ideal due to the difficulties in growth periodicity, wedging rings, and cross-dating problems (Worbes 2002; Groenendijk et al. 2014). Although a great amount of NPPs are situated near the sea or rivers for the convenience of cooling systems, few studies examined the ^{14}C in the fresh and/or seawater (Magnusson et al. 2008; Vincze et al. 2009; Wang et al. 2014). Before this study, coral ^{14}C as a tracer to evaluate the radionuclide release of NPPs had not been reported.

In this study, we tested ^{14}C values and elemental ratios in a coral from Daya Bay to see the impact from NPPs on ^{14}C levels and SST since the NPPs' operations and we would assess the ^{14}C record in coral as an alternative archive of radionuclide release from NPPs.

MATERIALS AND METHODS

Study Site

Daya Bay is located at 22°30′–22°50′N, 114°30′–114°50′E, to the north of the South China Sea (SCS) (Figure 1). It is a semi-enclosed bay with a steep slope and an area of ~600 km^2. Daya Bay is a typical marginal sea environment under strong human impacts. Both the agriculture and industry are dramatically increasing due to the urbanization in South China (Morton and Blackmore 2001). The lowest temperature (~14°C) appears in January or February, while the highest (~30°C) is in July or August (Chen et al. 2011b). The average annual precipitation in Daya Bay is 1920 mm, which mainly occurs during April to August, accounting for ~76% of the total annual precipitation. The predominant wind in this area is east-southeast and the secondary wind is north. The natural environment in Daya Bay is a good habitat for diverse corals. With the construction of NPPs and regional urbanization, corals have become less and less in Daya Bay (Wang et al. 2004).

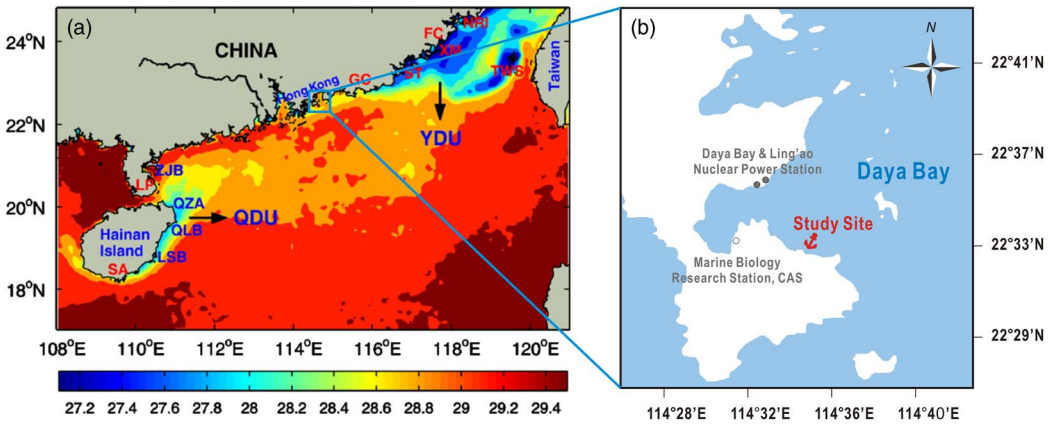

Figure 1 (a) The climatologically summer SST in the northern South China Sea (Jing et al. 2009); (b) sampling site and NPP locations in Daya Bay: the anchor icon indicates the coral sampling site, and the solid gray circles mark the sites of DNPP and LNPP, respectively.

Sample Preparation and Measurement

A living *Porites* coral was collected near Yangmeikeng in the summer of 2005, as shown in Figure 1. The sampling site is ~30 m away from the coast with a water depth of 5 m. It is ~7 km away from DNPP and LNPP. The organic material was removed and then the coral was cut into 1-cm-thick slabs. An x-ray print was used to locate the annual bands (Figure 2). The slab with clearest growth bands was soaked in 10% H_2O_2 solvent for 24 hr and 0.1 N HNO_3 for 15 min to eliminate any organic remains and adherent contaminants (Mitsuguchi et al. 2001). The slab was then cleaned with Milli-Q water in an ultrasonic bath for 20 min, repeating for 3 times. The coral slab then was subsampled at an interval of 1 mm to get a monthly resolution along the major growth axis by a dental-type drill (Griffin and Druffel 1985).

About 1 mg from each sample was prepared for Sr/Ca and Mg/Ca analysis. The aliquot was dissolved in 1% HNO_3 and diluted to 10,000 times. The elemental ratios were measured by a Varian Vista Pro Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (Wei et al. 2004). The measurement followed the method based on Schrag (1999), with an internal standard of a modern *Porites lutea* coral at intervals for monitoring and result correction. The external precision of Sr/Ca and Mg/Ca ratio are 0.3% and 0.2%, respectively. Sr/Ca and Mg/Ca ratios were reported after the correction of instrumental drift with the internal standard (Wei et al. 2004, 2007).

About four continuous monthly samples were mixed to get approximately 1 mg carbon for the ^{14}C analysis. The mixed sample was pumped down and converted to CO_2 by acidification with 85% ortho-phosphoric acid (Griffin and Druffel 1985). Then, the CO_2 was purified on a vacuum

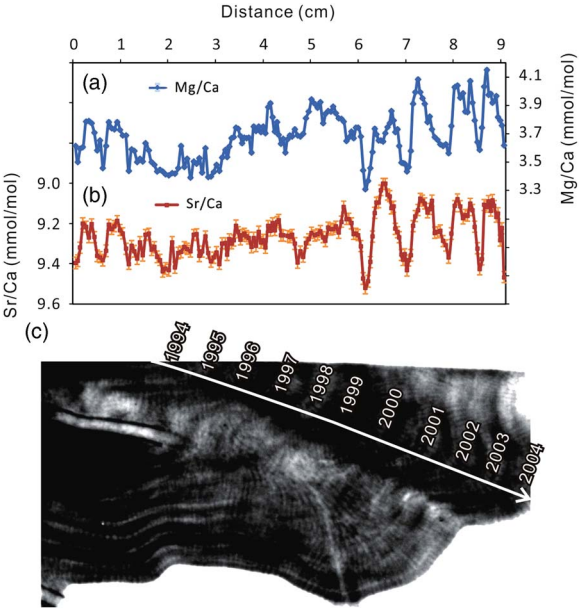

Figure 2 (a) The Mg/Ca ratio variations with distance; (b) the Sr/Ca ratio variations with distance; (c) x-ray positive print of *Porites* coral from Daya Bay (the white line is the section line for subsampling).

line in the AMS-^{14}C lab in Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. We used the zinc reduction method to convert CO_2 to graphite according to Xu et al. (2007). Finally, the graphite was analyzed by accelerator mass spectrometry (AMS) at Peking University (Liu et al. 2007). The ^{14}C results are reported as pMC and age corrected $\Delta^{14}C$ (‰) (Stuiver and Polach 1977). A modern coral standard of *Porites* which was run repeatedly indicated the total uncertainty is ±0.45 (pMC).

RESULTS

Sr/Ca and Mg/Ca Records

The Mg/Ca and Sr/Ca ratios with error bars are shown in Figure 2. The x-axis is the distance from the bottom, along the section line to the top of the coral. The Sr/Ca ratio has a negative relation to SST, while Mg/Ca has a positive relationship with SST. The cycles in Sr/Ca and Mg/Ca ratio indicate the annual SST cycles (Beck et al. 1992; Mitsuguchi et al. 1996; Deng et al. 2010). Most elemental ratios demonstrate the annual periodicity, which helps identify the chronology for this coral. The x-ray print also shows annual density bands, which can also be used to identify the growth years. Based on elemental ratios and the x-ray print, we found a continuous 11-yr record of Mg/Ca and Sr/Ca ratios in this coral, from 1994 to 2005. Furthermore, we also fine-tuned the Sr/Ca variability to the instrumental SST variation from Zhelang Observation Station, which is 80 km from the study site (Chen et al. 2013). The Sr/Ca, Mg/Ca, and ^{14}C data using a fine-tuned age model are shown in Figure 3. Due to the high growth rate of coral in summer and low growth rate in winter, the age assignment has an error of 2 months according to pervious work (Bagnato et al. 2004; Guilderson et al. 2004).

To remove the seasonal signals in the elemental ratios, low-pass filtering with a cutoff frequency of 0.5 Hz was performed (dark blue line and dark red line in Figure 3 in the online version). Those curves show the general trend of elemental ratio variations. Both the low-pass filtered

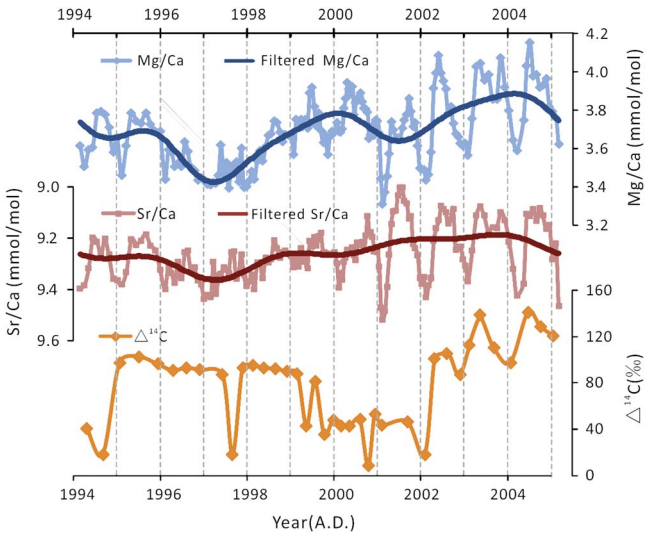

Figure 3 The Mg/Ca, Sr/Ca ratios and $\Delta^{14}C$ value with time in the coral from Daya Bay. A low-pass filter (cutoff frequency is 0.5) is used to get the signal of elemental ratios without seasonal signals. The dark blue line (top) is the filtered Mg/Ca curve, while the dark red line (middle) is the filtered Sr/Ca curve. (Colors refer to online version.)

Mg/Ca and Sr/Ca variations show a gradual increase from 1994 to 2005. In addition, the filtered Mg/Ca curve presents a cycle change with the period of 4–5 yr.

^{14}C Records

Radiocarbon variation shows three distinguishable stages (Figure 3). The first stage is from 1994 to 1999, in which the $\Delta^{14}C$ values increased rapidly in 1994 and stayed at a high level (average at 78‰) until 1999. Then the $\Delta^{14}C$ dropped from 1999 and remained low until 2002, which is the second stage with a mean $\Delta^{14}C$ value of 39‰. In the second stage, there was a moderate seasonal variation with amplitude of ~40‰. The last stage is from 2002 to 2005. The $\Delta^{14}C$ rose dramatically at the middle of 2002 and had stronger seasonal cycles. The average $\Delta^{14}C$ value was 117‰ and the seasonal difference reached up to ~50‰. The seasonal $\Delta^{14}C$ results were always low in winter but higher in summer (2000–2005). The correlation between the $\Delta^{14}C$ and elemental ratios was found to be negligible. All the original $\Delta^{14}C$ results are reported in Table 2.

DISCUSSION

SST Variations in Daya Bay

Both the filtered Mg/Ca and Sr/Ca curves had low values during 1996–1998 (Figure 3). The seasonal difference in elemental ratios was much smaller at this time. We believe these results are consistent with the El Niño event in 1997–1998, suggesting that the SST in Daya Bay could be influenced by extreme climate events. The Pacific Decadal Oscillation (PDO) index is established on the monthly January-February-March SST anomalies in the Pacific Ocean (north of 20°) (Mantua et al. 1997). During the positive phase of PDO, the east Pacific is warmer while the western part is cooler, and vice versa. Thus, we compared the Mg/Ca ratio in coral

Table 2 Radiocarbon results of coral from Daya Bay.

Lab ID	Tuned age (AD)	pMC ± 1σ	Δ ^{14}C (‰) ±1σ	Lab ID	Tuned age (AD)	pMC ± 1σ	Δ ^{14}C (‰) ±1σ
GZ098	2005.06	112.70 ± 0.46	119.7 ± 4.6	GZ165	1999.78	104.15 ± 0.33	35.4 ± 3.3
GZ099	2004.76	113.54 ± 0.50	128.0 ± 5.0	GZ166	1999.57	108.70 ± 0.34	80.6 ± 3.4
GZ100	2004.47	114.74 ± 0.47	139.9 ± 4.7	GZ172	1999.37	104.85 ± 0.33	42.3 ± 3.3
GZ112	2004.07	110.40 ± 0.88	96.9 ± 8.8	GZ173	1999.16	109.40 ± 0.34	87.5 ± 3.4
GZ113	2003.69	111.67 ± 0.46	109.6 ± 4.6	GZ174	1998.92	109.58 ± 0.43	89.5 ± 4.3
GZ114	2003.42	114.54 ± 0.46	138.1 ± 4.6	GZ175	1998.66	109.82 ± 0.35	91.8 ± 3.5
GZ115	2003.20	111.89 ± 0.65	111.9 ± 6.5	GZ178	1998.40	109.86 ± 0.33	92.2 ± 3.3
GZ116	2002.97	109.37 ± 0.49	86.8 ± 4.9	GZ179	1998.14	110.11 ± 0.34	94.7 ± 3.4
GZ117	2002.64	111.14 ± 0.63	104.4 ± 6.3	GZ176	1997.91	109.88 ± 0.34	92.6 ± 3.4
GZ118	2002.37	110.73 ± 0.50	100.4 ± 5.0	GZ191	1997.67	102.38 ± 0.31	18.0 ± 3.1
GZ160	2002.10	102.44 ± 0.33	18.1 ± 3.3	GZ180	1997.43	109.26 ± 0.45	86.4 ± 4.5
GZ134	2001.70	105.27 ± 0.48	46.2 ± 4.8	GZ181	1996.91	109.68 ± 0.45	90.7 ± 4.5
GZ157	2001.10	104.98 ± 0.41	43.5 ± 4.1	GZ182	1996.61	109.85 ± 0.45	92.4 ± 4.5
GZ158	2000.95	105.91 ± 0.34	52.7 ± 3.4	GZ183	1996.31	109.62 ± 0.45	90.1 ± 4.5
GZ159	2000.79	101.42 ± 0.34	8.1 ± 3.4	GZ184	1995.95	110.18 ± 0.45	95.8 ± 4.5
GZ161	2000.60	105.44 ± 0.33	48.0 ± 3.3	GZ185	1995.51	110.80 ± 0.45	102.0 ± 4.5
GZ162	2000.37	104.90 ± 0.34	42.7 ± 3.4	GZ186	1995.08	110.26 ± 0.33	96.8 ± 3.3
GZ163	2000.18	104.86 ± 0.34	42.4 ± 3.4	GZ189	1994.69	102.36 ± 0.30	18.2 ± 3.0
GZ164	1999.99	105.41 ± 0.45	47.9 ± 4.5	GZ190	1994.31	104.59 ± 0.32	40.3 ± 3.2

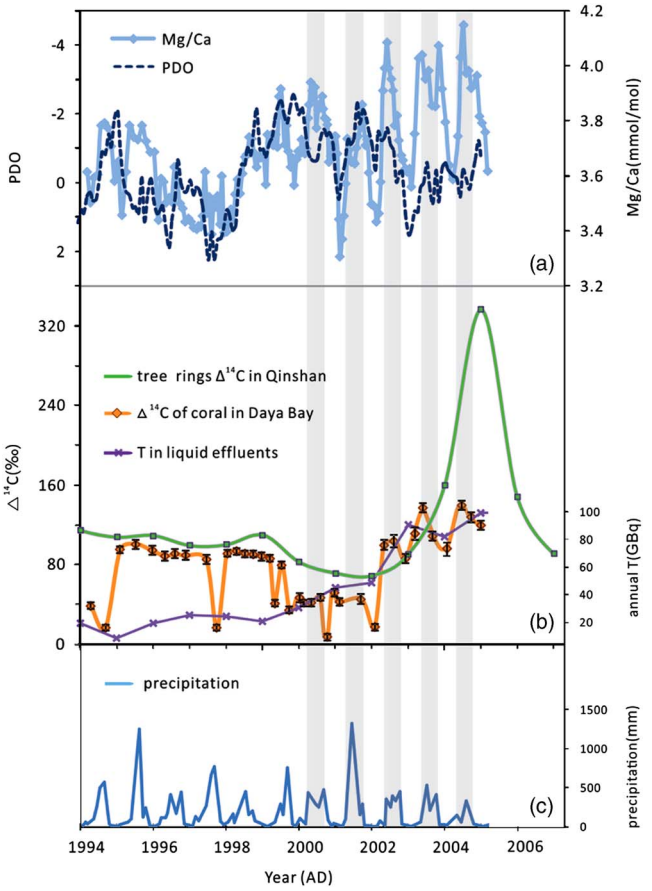

Figure 4 (a) Comparison between Mg/Ca ratios in the coral from Daya Bay and PDO index from 1994 to 2004 (see http://research.jisao.washington.edu/pdo/PDO.latest); (b) the $\Delta^{14}C$ and T records in NPPs in Daya Bay, and $\Delta^{14}C$ record in QNPPs: the (orange) diamond with error bars is the $\Delta^{14}C$ value, the (purple) cross is the T in the liquid release, and the (green) square is the $\Delta^{14}C$ record in the tree ring from QNPPs (Wang et al. 2012); (c) seasonal precipitation record from Daya Bay weather station (22°31′N, 114°31′E) (Chen et al. 2011a). (Colors refer to online version.)

with the PDO index, to assess the correlation between SST in Daya Bay and the global climate oscillation (Figure 4). The Mg/Ca ratio in Daya Bay had a significant negative correlation with PDO before 2002, indicating that the SST in Daya Bay was consistent with the variability of PDO before 2002. However, this correlation changed after 2002. A higher Mg/Ca ratio in the coral indicated unusually higher SST in Daya Bay after 2002. The inconsistency between the Mg/Ca ratio and PDO is possibly a result of the warm-water discharge from NPPs in 2002.

$\Delta^{14}C$ Variation with Climate Variability

Deep seawater is isolated from the atmosphere and usually has lower ^{14}C concentration due to the radioactive decay. Previous studies showed that low radiocarbon concentration in corals was usually caused by upwelling (Grumet et al. 2002; Druffel et al. 2004; Mitsuguchi et al. 2004;

Druffel et al. 2007). Figure 1 shows the upwelling areas in the northern South China Sea, using a model based on SST and wind data (Jing et al. 2009). One of the main upwelling areas in the northern South China Sea is east of Hainan Island and the other is in the Taiwan Strait (blue areas in Figure 1). Daya Bay is in neither of these areas. So, the low values of $\Delta^{14}C$ in 2000–2001 as well as those in 1994 should be the regional background level, rather than a lower level caused by upwelling in Daya Bay.

Oceanic circulations driven by climate change can also regulate the ^{14}C concentration in seawater DIC (Toggweiler et al. 1991; Southon et al. 2002; Druffel et al. 2004). Many coral records from the Pacific area show that PDO is the main control of ^{14}C variation in seawater DIC (Grottoli et al. 2003; Druffel et al. 2014). As illustrated in Figure 4, the $\Delta^{14}C$ results in this study show an insignificant correlation with the PDO index, revealing that oceanic circulation has limited influence on the change of $\Delta^{14}C$ values in seawater in Daya Bay.

Radionuclide Release from NPPs in Daya Bay

Since the oceanic circulation is not the primary reason, the anthropogenic ^{14}C release from nearby NPPs is probably the cause of the increase of $\Delta^{14}C$ in our coral record. There are two significant increases in the coral $\Delta^{14}C$ record from Daya Bay: one is in 1994 and the other is in 2002. According to the operation date of NPPs in Daya Bay (Table 1), these increases happened close to the operation date of DNPP2 in 1994, and the opening date of LNPPI1 and LNPPI2 in 2002, respectively. Wang et al. (2012) reported an abrupt increase of $\Delta^{14}C$ in the tree ring record due to the operation of Plant III in QNPP in 2003, suggesting the radionuclide releases likely happened when new reactors began operations (Figure 4).

However, QNPP III is a HWR, which has more $^{4}CO_2$ released in liquid and gaseous effluents. There are few reports of a high concentration of $^{14}CO_2$ being released from PWR type plants. In order to observe if the high $\Delta^{14}C$ events are caused by the release from PWR NPPs, we need to compare the $\Delta^{14}C$ results with the radionuclide release records from the NPPs. Since the ^{14}C in liquid and gaseous effluents was not required to be reported prior to 2013 in Daya Bay, we needed to find another proxy to represent the radiocarbon release variation from the NPPs in Daya Bay for the period from 1994 to 2005. Among the available records of radionuclide release of noble gas, iodine and particles in gas effluents and tritium in liquid effluents (https://www.hknuclear.com/dayaperf/releases/pages/radioactive.aspx?lang=sc), only the tritium in liquid showed a good agreement with the radiocarbon release trend from NPPs. Figure 5 shows the variation of tritium in liquid effluents and radiocarbon both in gaseous and liquid effluents from 2013 to 2015. The correlation coefficient of tritium in liquid effluents and radiocarbon in gaseous effluents is $r = -0.52$ ($N = 36$, $p = 0.0012$), while the one of tritium and ^{14}C in liquid effluents is $r = 0.83$ ($N = 36$, $p < 0.001$). That indicates tritium in liquid effluents has a moderate correlation with radiocarbon in gaseous effluents but a very strong positive correlation with the radiocarbon in liquid effluents. Hence, we can use the tritium in liquid effluent as an alternative proxy for radiocarbon in liquid effluents from 1994 to 2005.

In Figure 4b, the tritium in liquid effluents increased slowly from 1994 to 2001. The value of tritium in liquid effluents was lower than 50 TBq before 2001. However, there is an abrupt rise from 50 TBq to 90 TBq after 2002. Therefore, the radionuclide release (e.g. T and ^{14}C) from NPPs indeed increased when the new reactors started operation, similar to the observation at the QNPPs (Wang et al. 2012). Because Daya Bay is a semi-closed area and intercepted by land to the west of NPPs, the liquid effluents from NPPs will eventually flow to the south and east part of the bay, at the location of our study site and the coral could be easily influenced by the radiocarbon released from NPPs.

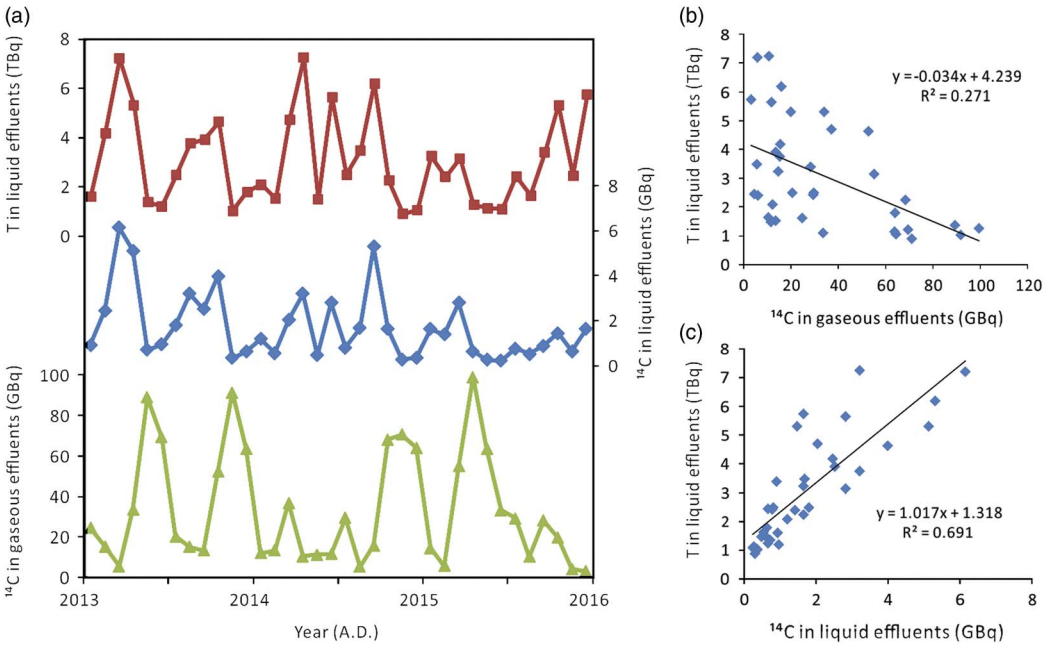

Figure 5 (a) Monthly radiocarbon and tritium release records from NPPs in Daya Bay 2013–2015; (b) tritium in liquid effluents versus ^{14}C in gaseous effluents; (c) tritium in liquid effluents versus ^{14}C in liquid effluents (accessed from https://www.hknuclear.com/dayaperf/releases/pages/radioactive.aspx).

According to the LNPP construction history, the water channel was moved eastward after 1999 (Ji and Zhang 2004). This reduced the influence from liquid radionuclide release to the sampling site and lowered the $\Delta^{14}C$ value. That is why the $\Delta^{14}C$ values in 2000 and 2001 were much lower, close to the background level in 1994. Such a reduction of radionuclide release to the marine life was also revealed by ^{110}Ag in a *Sargassum* sample from western Daya Bay (Ji and Zhang 2004). Based on the mean values of three stages, the $\Delta^{14}C$ level in seawater DIC increased by ~80‰ in 1994, then decreased by ~40‰ in 1999 and then increased by ~80‰ again in 2002. The two increases have similar excess $\Delta^{14}C$ of ~80‰, which is probably caused by effluent from the NPPs. According to Equation (6), the excess $\Delta^{14}C$ of ~80‰ is equal to the specific activity of ~18 Bq/Kg C.

$$A = \frac{\mathrm{pMC}}{100\,\%} \cdot \left(\frac{1+\frac{\delta^{13}C}{1000}}{0.975}\right)^2 \cdot e^{\left(\frac{1950-y}{8267}\right)} \cdot 226\mathrm{Bq/kg\,C} \quad (6)$$

Additionally, the seasonal variation of $\Delta^{14}C$ in coral shows a characteristic of high values in summer. The possible reasons could be upwelling, wind, precipitation and seasonal variation in the radiocarbon release from NPPs. According to previous studies, the upwelling has limited influence on Daya Bay (Figure 1) (Chen et al. 2011; Xu et al. 2003). In Figure 5, the ^{14}C releases in gaseous and liquid effluents from NPPs do not appear to have a similar seasonal change to the $\Delta^{14}C$ value in the coral. The wind is dominated by east-southeast wind in summer and a north wind in winter due to the Asian Monsoon. Owing to the land barrier to the west, the surface water with high $\Delta^{14}C$ values should sink in western Daya Bay and enhance the air-sea exchange in summer, resulting in a higher $\Delta^{14}C$ recorded in corals. On the other hand, the north wind in winter will draw the surface seawater away from Daya Bay, bring the compensating

current with lower $\Delta^{14}C$ value from deep layer into the study site. Additionally, the precipitation in summer is another possible cause, which can bring the ^{14}C in air into the seawater. As shown in Figure 5, the ^{14}C in airborne effluents should be ten times higher than that in liquid effluents. Although the relative ratio of $^{14}CO_2$ in the airborne effluents is low (5–25%), the absolute concentration of $^{14}CO_2$, which could be stripped into the seawater, should be higher than the value in seawater without this effect. Both wind and precipitation could lead to the high $\Delta^{14}C$ in summer, and it is hard to conclude which is the main reason for the seasonal $\Delta^{14}C$ variation pattern in Daya Bay.

CONCLUSION

The Mg/Ca and Sr/Ca records in coral from Daya Bay reveal that the SST is gradually increasing from 1994 to 2005, except the El Nino year in 1997–1998. The SST in Daya Bay had a good correlation with PDO until the LNPP began operation in 2002, which caused an increased SST in Daya Bay. The $\Delta^{14}C$ value of DIC in nearby seawater was sensitive to the increased $\Delta^{14}C$ release from NPPs when the reactors began operating in 1994 and 2002, respectively. The ^{14}C release from NPPs has a strong and long influence on seawater due to the slow exchange of seawater in semi-closed Daya Bay with other marine carbon reservoirs. The relative increase of radiocarbon in the study site was about ~80‰ in $\Delta^{14}C$, equivalent to 18 Bq/kgC in specific activity. The reason for the high $\Delta^{14}C$ value in summer is unclear. We propose that it is linked with the wind and/or precipitation. The examination of elemental ratios and $\Delta^{14}C$ value in the coral from Daya Bay shows great potential in monitoring the environmental and radiation effects from NPPs, especially for the NPPs without a ^{14}C release record.

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