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Combination of field-based natural gamma radiation and laboratory-based HPGe gamma spectrometry to investigate the natural radionuclides of a long coral core (928 m) in the South China Sea

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1 Introduction

Natural gamma radiation (NGR) is a classical geophysical method and is widely applied in stratigraphic classification and other geotechnology. The total counting rate of gamma photons emitted from the natural radionuclides (^{238}U decay chain, ^{232}Th decay chain, and ^{40}K) is recorded as the NGR using field-based NaI gamma spectrometry with a high depth resolution (1 data per 1 m in our coral core). The natural radionuclides are ultimately originated from Earth's interior, where radiogenic heat is generating from the decay of these radionuclides with a contribution of ~50% of total heat flow from Earth's interior to surface (Dye, 2012). The natural radionuclides in the mantle will be redistributed during the formation of rocks and minerals with variable concentrations in the crust (Van Schmus, 1995). Therefore, the NGR is used to estimate shale content, search for uranium mine, indentify lithological profile and clay mineral typing (Schön, 2011).

Generally, the activities of ^{40}K, ^{238}U, and ^{232}Th are quantified at the photopeaks of 1461 keV, 1756 keV, and 2615 keV, respectively, during the applications of spectrometry of the NGR (Van Schmus, 1995; Vleeschouwer et al., 2017). It is noted that the activities of ^{238}U and ^{232}Th are calculated according to their progenies of ^{214}Bi (1756 keV) and ^{208}Tl (2615 keV,) on the basis of the assumption of secular equilibrium in ^{238}U and ^{232}Th decay chains. The secular equilibrium is generally satisfied for most holes during the measurement of the NGR in continental and marine sediment (Vasiliev et al., 2011; Vleeschouwer et al., 2017). However, the disequilibrium between ^{238}U and its progenies may occur due to the distinct chemical behaviours of radionuclides in 238U decay chain and long half-life of 234U (2.44×105 a), 230Th (7.7×104 a), and 226Ra (1600 a) to reach equilibrium (Lin et al., 2018). Therefore, the activity of ^{238}U should be quantified by its daughter radionuclide ^{234}Th with the photopeak of 63.3 keV rather than by its daughter radionuclide ^{214}Bi with the photopeak of 1756 keV in the disequilibrium condition (Huy and Luyen, 2004; Lin et al., 2018; Liu and Lin, 2018).

However, the photopeak of <150 keV is generally discarded due to high background in the low energy interval and low energy resolution of NaI gamma spectrometry, constraining ^{238}U quantification using spectrometry of the NGR. The laboratory-based High Purity Germanium (HPGe) gamma spectrometry shielding by 15 mm old lead is generally used to calculate ^{238}U activity due to its low background of the low energy interval and high energy resolution (Lin et al., 2018; Liu and Lin, 2018). Although the concentration of ^{238}U is widely measured using mass spectrometry, chemical separation is complicated and time-consuming relative to HPGe gamma spectrometry (Zhao et al., 2009). Other natural radionuclides (^{226}Ra, ^{40}K, ^{228}Ra, etc.) can also be simultaneously measured using HPGe gamma spectrometry, while minimum detection activity of radium isotope is high using mass spectrometry relative to other radiometric method (Jia and Jia, 2012). It is also noted that the measurement using the laboratory-based HPGe gamma spectrometry is time-consuming relative to the measurement using the field-based NGR.

In the present study, the combination of the field-based

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NGR and the laboratory-based HPGe gamma spectrometry was applied to simultaneously investigate the natural radionuclides in a long coral core (928 m) of well Chenke-2 in the Xisha Islands, South China Sea (SCS) (Li et al., 2017). We exhibited the total counting rate of the NGR and the actual activities of the natural radionuclides (^{238}U, ^{226}Ra, ^{228}Ra, and ^{40}K) for the first time in the SCS. The vertical distribution of the NGR of the long coral core and its mechanism was discussed. A deficit of ^{226}Ra relative to ^{238}U was observed and interpreted using this combination of the field-based NaI gamma spectrometry and the laboratory-based HPGe gamma spectrometry. In addition to the cross-checking between the NGR and HPGe gamma spectrometry, the characteristics of high depth resolution of the NGR and high accuracy of the HPGe gamma spectrometry can be combined to provide more information. This analytical strategy may provide insights to other holes in the future.

2 Materials and Method

In this study, a long coral core named well Chenke-2 with a length of 928 m was sampled during April to December in 2013. The well Chenke-2 (16°27′11″N, 111°42′41″E) is located in the Yongle Atoll in the SCS (Li et al., 2017). The NGR was measured by the field-based NaI gamma spectrometry with the data resolution of 1 m. The laboratory-based HPGe gamma spectrometry (Canberra BE6530) was operated in Guangxi University after picking sample with a weight of 20 g. The activities of natural radionuclides were calibrated by standard materials (IAEA-385) provided by International Atomic Energy Agency (Lin et al., 2018; Liu and Lin, 2018). The instrumental background and detection efficiency were periodically measured to guarantee the data quality. Additionally, we also participated in and passed the proficiency test of radionuclides (^{210}Pb, ^{238}U, ^{226}Ra, ^{228}Ra, ^{228}Th, ^{40}K, and ^{137}Cs) in marine sediment organized by the National Marine Environmental Monitoring Centre of China in October 2017.

3 Results and Discussion

The NGR was measured using NaI gamma spectrometry and exhibited in the Fig. 1. The value of the NGR had a range of 0 cps to 129 cps. We observed abnormally high NGR at the bottom of the core, which had grey and black color relative to the overlying samples with white color. The results of the NGR were confirmed by the rock slice method. The white color was related to the biogenic carbonate rock (limestone and dolomite) with low activities of the natural radionuclides, while the grey and black color referred to the igneous rock with high activities of the natural radionuclides (Lin et al., 2018).

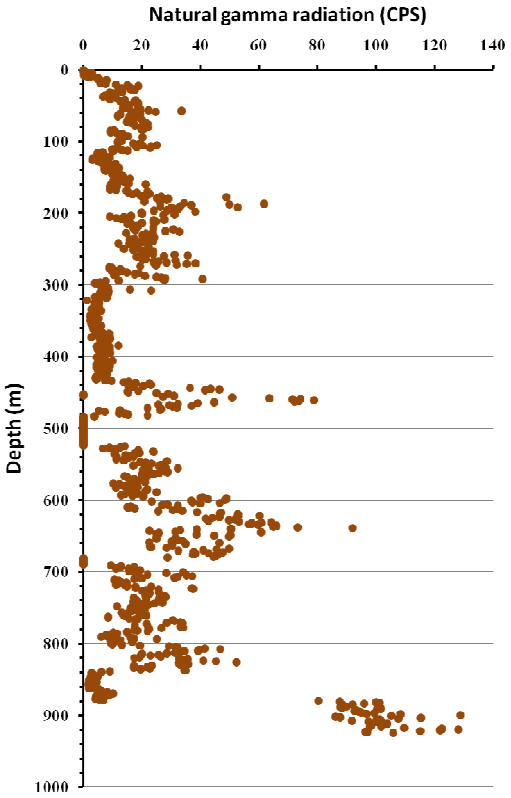

Fig 1. The vertical profile of the NGR of a long coral core in the SCS. The unit of the NGR is expressed as counts per second (cps).

The actual activities of the natural radionuclides (^{238}U, ^{226}Ra, ^{228}Ra, and ^{40}K) were simultaneously detected for the upper samples (2 m-28 m) using the laboratory-based HPGe gamma spectrometry (Fig. 2). The activities of ^{238}U, ^{226}Ra, ^{228}Ra, and ^{40}K were in the range of 11.4 Bq/kg-32.1 Bq/kg, 0.5 Bq/kg-19.6 Bq/kg, 1.7 Bq/kg-5.5 Bq/kg, and 0.4 Bq/kg-10.3 Bq/kg, respectively. The activity of ^{226}Ra gradually increased with the depth from 2 m to 12 m. It was noted that the ^{226}Ra/^{238}U disequilibrium was also observed from 2 m to 12 m (red rectangle in Fig. 2) relative to the equilibrium of ^{226}Ra and ^{238}U from 14 m to 28 m (green rectangle in Fig. 2). The ^{226}Ra/^{238}U disequilibrium was attributed to the process of coral calcification with the preferential uptaken of ^{238}U and discrimination of ^{230}Th in the aragonite structure (major contribution from coral skeleton) (Zhao et al., 2009). The equilibrium of ^{226}Ra and ^{238}U was reached along with the decay of ^{238}U and the ingrowth of ^{226}Ra. The ^{226}Ra/^{238}U disequilibrium cannot be observed with spectrometry of the field-based NaI gamma spectrometry.

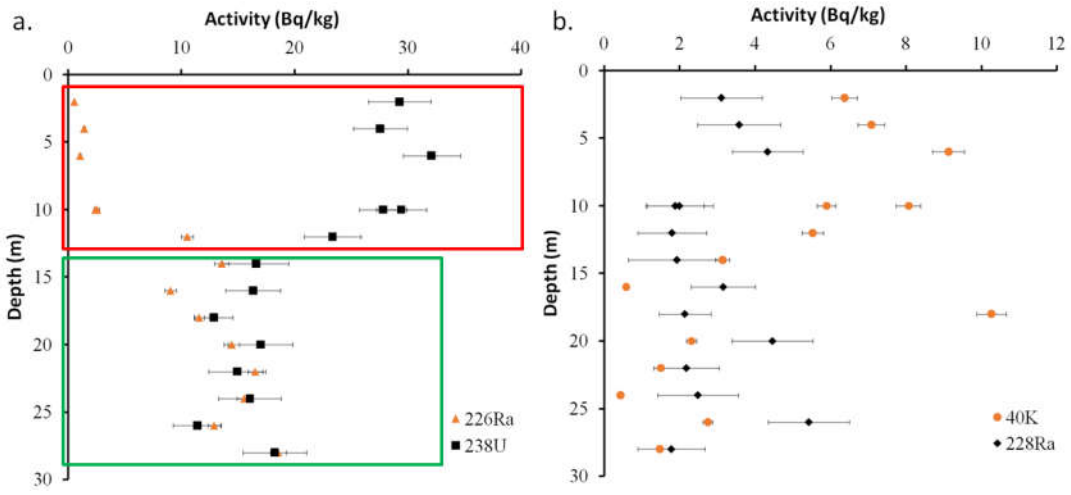

Fig.2 The vertical profile of ^{226}Ra, ^{238}U, ^{40}K, and ^{228}Ra for the upper sample (2 m-28 m) of a long coral core in the SCS. The unit of the activity is expressed as Bq/kg. The red rectangle indicates the disequilibrium between ^{226}Ra and ^{238}U, while the equilibrium between ^{226}Ra and ^{238}U is marked with the green rectangle.

To investigate the integrating radioactivity of the samples, radium equivalent activity (Ra_{eq}) was calculated according to Eq. 1 (Liu and Lin, 2018). The NGR is related to the total counting rate of the natural radionuclides. A comparison of the NGR and Ra_{eq} was represented in Fig. 3. The vertical profile the NGR derived from the field-based NGR had a similar trend with that of Ra_{eq} based on the laboratory-based HPGe gamma spectrometry, confirming reliability of the data after the cross-checking of the NGR and Ra_{eq}.

$$Ra_{eq}(Bq/kg)=A_{Ra}+1.43A_{Th}+0.077A_K \quad (1)$$

Where A_{Ra}, A_{Th}, and AK refers to the activities of ^{226}Ra, ^{228}Ra, and ^{40}K.

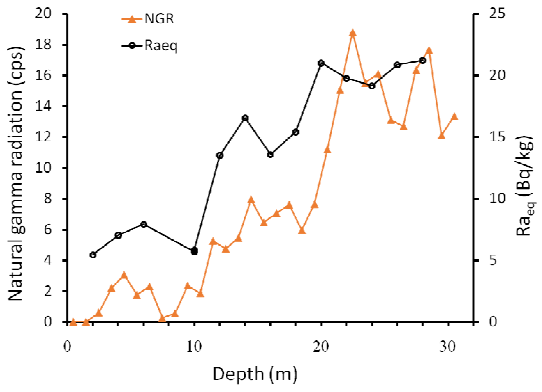

Fig.3 Similar trend between the NGR and Ra_{eq} of a long coral core in the SCS.

The positive linear relationship between ^{226}Ra and Ra_{eq} was displayed in Fig. 4a with a high value (0.93) of R^2.

Meanwhile, we had not observed any significant corelationship between Ra_{eq} and ^{228}Ra and ^{40}K (Fig. 4b and Fig. 4c). Therefore, the increasing trend of Ra_{eq} and the NGR should be attributed to the physical process of the ingrowth of ^{226}Ra in ^{238}U decay chain rather than diagenesis process and other natural processes related to climate variation.

It was noted that a negative relationship between Ra_{eq} and ^{238}U was observed in Fig. 4d. A decline in ^{238}U activity was indicated in Fig. 2a and may be attributed to the sea level fall during the last glacier period. The exposure of coral platform may benefit the corrosiveness of carbonate rock and mobility of ^{238}U by rain water during the glacier period (Banner et al., 1991). The physical process determined the vertical distribution of Ra_{eq}, while the vertical profile of ^{238}U was related to the chemical processes (rain water). Therefore, there was no casual relationship between Ra_{eq} and ^{238}U.

4 Conclusion

The NGR and the actual activities of natural radionuclides (^{238}U, ^{226}Ra, ^{228}Ra, and ^{40}K) were obtained for the first time in the SCS using the combined method of the field-based NGR and the laboratory-based HPGe gamma spectrometry. High value of the NGR was observed at the bottom depth of the coral core (880 m-927 m), attributing to the igneous rock with high activities of the natural radionuclides relative to the overlying biogenic carbonate rock (limestone and dolomite) with low activities of the natural radionuclides. The ^{226}Ra/^{238}U disequilibrium was clearly observed from 2 m-12 m relative to the equilibrium between ^{226}Ra and

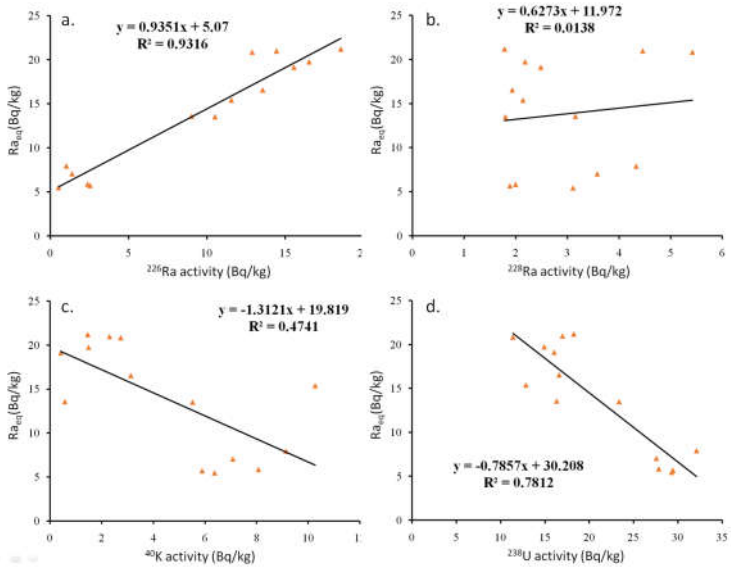

Fig.4 Relationship between Raeq and ^{226}Ra, ^{228}Ra, ^{40}K, and ^{238}U from the depth of 2 m to 28 m.

^{238}U from 14 m-28 m. The increasing trend of Ra_{eq} and the NGR from 2m to 28 m should be attributed to the physical process of the ingrowth of ^{226}Ra in ^{238}U decay chain rather than diagenesis process and other natural processes related to climate variation. The analytical strategy of combination of the field-based NGR with the characteristic of high depth resolution and the laboratory-based HPGe gamma spectrometry with the characteristic of high accuracy may provide insights to other holes in the future.

Acknowledgements

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