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Radiocarbon ages of different fractions of peat on coastal lowland of Bohai Bay: marine influence?*

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Abstract Peat in boreholes is the most important ^{14}C dating material used for constructing age framework. 20 bulk peat samples were collected from five boreholes, the ^{14}C ages of two fractions (organic sediment fraction and peat fraction) of the bulk peat samples were investigated by AMS-dating and which fraction is better to help construct an age framework for the boreholes were compared and discussed. The results indicated that the peat fraction give a good dating results sequence in the boreholes, compared with the corresponding organic sediment fraction. And the dating results of organic sediment fraction show 161–6 702 years older than corresponding peat fraction, which was caused by marine influence. Then, we suggest an experience formula as y=0.99x–466.5 by the correlation analysis for correcting the marine influenced organic sediment ages within the conventional ages between 4 000 to 9 000 yrs BP, and more study should be carried out for the AMS ^{14}C dating of the bulk organic sediments.

Keyword: coastal lowland of Bohai Bay; peat fraction; organic sediment fraction; AMS ^{14}C dating; marine influence

1 INTRODUCTION

Peat in boreholes is the most important ^{14}C dating material used for constructing age framework and the bulk peat samples can be divided into organic sediment fraction (OSF, almost the humin, humic acid and fulvic acid) (Cook et al., 1998) and corresponding peat fraction (PF, usually include the degraded plant, plant and charcoal) by sieving; However, the problem is that it is usually difficult to collect enough peat in bulk peat samples to date for the age framework construction of cores. At the mean while, the bulk organic faction is easier to collect from bulk peat samples, so the organic sediment fraction becomes an important material to construct age framework for cores.

For organic sediment fraction, most studies showing that different chemical fractions yield a different age. Although some research give suggestions on which chemical fraction is better, the results are different (Williams, 1989; Johnson et al., 1990; Hammond et al., 1991; Bartley and Chambers, 1992; Cook et al., 1998; Gulliksen et al., 1998; Waller et al., 2006). Shore et al. (1995) reported 127 radiocarbon dates, and the results from four columns of peat are highly variable and mutually inconsistent. The age results of the humic acid and the corresponding humin fractions showing that sometimes, the humic acid is 630 years younger than the humin fraction and sometimes, the humic acid is 1 210 years older than the humin fraction, even when a two sigma confidence is allowed. Brock et al. (2011) measured different chemical fractions (humin and humic acid) of a peat sample, the age results indicate that with increasing grain size, both the humin and humic acid ages

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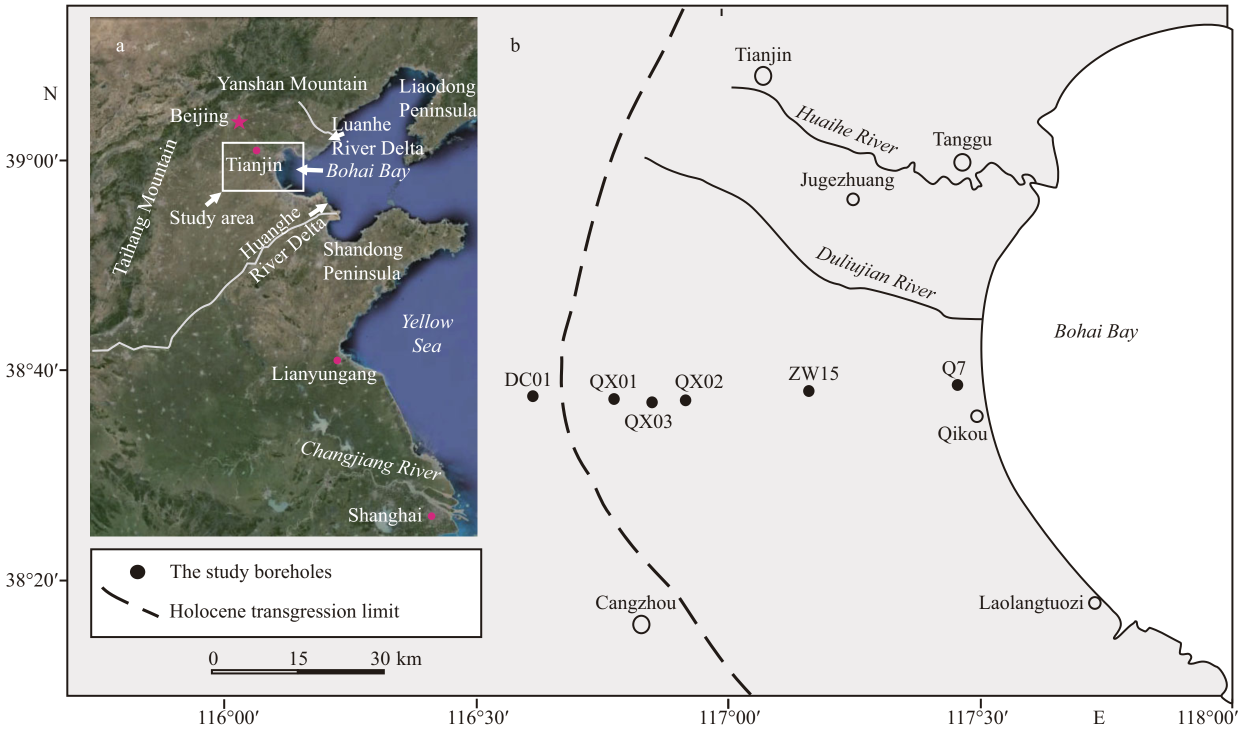

Fig.1 Sampling sites location on the west coast of Bohai Bay

increased and for all except one sample the humin acid fraction was older than the corresponding humic date. However, the sample containing the cryptotephra are still difficult to definitively decide which eruption is responsible for the observed ash horizon because of a spanned time period of 1 500 years.

Some study focus on measuring selected plants, certain grain size of peat, and they also given different suggestions (Törnqvist et al., 1992; Cook et al., 1998; Zhou et al., 2002; Blaauw et al., 2004). Blaauw et al. (2004) proposed a study on weather a reservoir effect was existence in bulk ^{14}C dates of raised bog peat, and can't confirm the existence of a reservoir effect reported by Kilian et al. in 1995 based on the ages comparison between bulk samples and the selected plant remains. Cook et al. (1998) found no evidence of variability in ^{14}C age due to pretreatment scheme or between different geochemical fractions of the peat. Zhou et al. (2002) suggest that the 60–180 μm fraction of a Holocene peat to date, as they regarded this as undegraded plant material which should be representative of the true age of the layer because that larger material could contain modern root material growing in form above and finer material could contain consist of mud, possibly containing chemical impurity. Törnqvist et al. (1992) compared dates of bulk fractions with similar materials removed roots, and found that the samples containing roots could be either younger or older than those without roots.

All the studies mentioned above try to figure out one thing that make peat sample give a high precision age; However, the results given by different researchers are really different, so more studies in different area and different environments are still needed.

In this paper, we investigated the ^{14}C ages of two sample types (organic sediment fraction and peat fraction) collected from bulk peat samples in boreholes, in order to find out which fraction is better to help construct an age framework for the boreholes based on sedimentary petrology; Moreover, ^{14}C data of organic sediment fraction and peat fraction were compared, in order to find out the reason that cause the age difference between the two fractions.

2 STUDY SITE

The coastal lowland of Bohai Bay is on the west coast of Bohai Sea. The Bohai Sea is connected to the northern Yellow Sea and is a semi-enclosed inland sea of China (Fig.1). The elevation of the coastal lowland is less than +10 m. With the sea level rising after Last Glacial Maximum, the sea water maximum intruded into the inland of Bohai Bay in 6 000–7 000 BP. A widely distributed layer of basal peat was forming, which has been a widely used material for ^{14}C dating in order to construct the age framework for boreholes collected from this area.

Our boreholes are apart 80–5 km from the modern coastline, where is crossing the boundary of the Holocene transgression maximum. Borehole DC01 was taken from the inland of this boundary and borehole QX01 was taken near this boundary. Boreholes QX03, QX02, ZW15 and Q7 were taken from landward to the seaward of this boundary (Fig.1).

3 MATERIAL AND METHOD

3.1 Sampling

20 bulk peat samples (1–2 cm thickness each samples) were collected for AMS ^{14}C dating from five boreholes (Fig.2). After pretreatment in lab, the bulk peat samples were divided into two fractions, one is organic sediment fraction (OSF), and the other is the corresponding peat fractions (PF). Totally, 40 sub-samples were measured.

3.2 Pretreatment of the samples for AMS ^{14}C dating

First, the bulk samples were sieved to 180 microns to remove any plant macrofossils (usually roots). The fraction of the sediments passed the sieve was called “organic sediment fraction” which is composed of any non-acid soluble organics such as some fulvic acids, humic acids and humins. The fraction of the sediments above the sieve was called “peat fraction” that composed of uncharred degraded plant, but since it was so degraded and not easily identifiable as a specific plant remains we choose to leave it listed as peat fraction (Table 1). All the samples were measured in BETA radiocarbon dating Lab, and the pretreatments of organic sediment fraction and peat fraction to our samples were used Beta standard methods. And then calibrate with the soft of calib 7.1.

Acid washes for the organic sediment fraction The “organic sediment fraction” are leached with hot HCl (~80°C) with 0.1 to 1.0 N concentration of HCl depending on the sediment type, amount of $CaCO_3$ present and if the $CaCO_3$ present is composed of a simple carbonate like $CaCO_3$ or something more resistant like Dolomite. Again depending on the above factors of the sediment, the number and length of time of the acid leaches will vary to insure that all of the $CaCO_3$ has been eliminated prior to the dating taking place. This “organic sediment fraction” contains both humic and the humin fractions. After drying at 100°C for 12–24 h a portion is tested with concertrated HCl to ensure the complete removal of any carbonates.

Acid/alkali/acid washes for the peat fraction Peat fraction include plant, charcoal, fibrous peat, etc are treated with 0.1 to 1.0 N HCl for 1–4 h at ~80°C (again concentration and application times may vary depending on if $CaCO_3$ is present or not), rinsed neutral, then treated with 1% to 2% NaOH at 80°C for a few minutes to up to 4 h (again how much alkali and for how long is unique to each sample, it is given as much alkali for as long as is possible to insure the complete removal of any humic acids and so that sufficient sample was left for dating). If possible (depending on the sample size and preservation) the NaOH leaches are applied 2–3 times with rinsing in-between to neutrality before the next application. When the alkali extractions have been completed, then 0.5 N HCl is applied at ~80°C for a minimum of 1 h prior to being rinsed neutral and dried at 70–100°C for 2–24 h.

4 RESULT

The radiocarbon dates of the organic sediment fraction and peat fraction are listed in Table 1, which contains material types, applied pretreatments, $^{13}C/^{12}C$, conventional ages corrected by isotopic fractionation using $^{13}C/^{12}C$, two-sigma calendar calibrated ages.

For borehole DC01, the dating results in the depth of 8.4 m give a very same age by organic sediment fraction and corresponding peat fraction, the age are 6 560±40 yrs BP and 6 590±40 yrs BP.

For borehole QX01, peat fraction gives a continuous age without disturbation from bottom to up, which is 7 200±30 → 7 010±30 → 6 220±40 → 6 030±40 → 5 830±30 yrs BP. Corresponding organic fractions give a wholly continuous age with disturbation, which is 7 480±40 → 7 210±40 → 7 350±40 → 6 200±30 → 6 120±40 yrs BP.

For borehole QX03, peat fraction gives a continuous age without disturbation from bottom to top layer, which is 7 280±40 → 6 690±40 → 6 410±40 yrs BP. Corresponding organic fractions give a wholly continuous age with disturbation, which is 7 570±40 → 7 230±40 → 7 480±40 yrs BP.

For borehole QX02, peat fraction gives a continuous age without disturbation from bottom to top layer, which is 7 140±40 → 7 150±40 → 7 020±30 → 6 600±30 → 6 350±30 yrs BP. Corresponding organic fractions give a wholly continuous age with disturbation, which is 7 470±40 → 8 130±40 → 7 370±40 → 7 130±40 → 6 910±40 yrs BP.

For borehole ZW15, peat fraction gives a continuous age with little disturbation from bottom to

Table 1 A list of dating results by AMS ^{14}C dating method

Core number	Depth (m)	Beta number	Material and pretreatment	$^{13}C/^{12}C$ (‰)	Conventional age (yrs BP)	Calibrated age (cal yrs BP) (2 sigma range)	Median age (cal yrs BP)	Difference (yrs)
DC01	8.4	331452	Bulk organic fraction: acid washes	-27.0	6 560±40	7 562–7 536, 7 517–7 422	7 466	-21
		329636	Peat fraction: acid/alkali/acid	-26.8	6 590±40	7 565–7 531, 7 523–7 430	7 487	
QX01	8.2	331456	Bulk organic fraction: acid washes	-24.5	6 120±40	7 157–6 902	7 005	358
		329641	Peat fraction: acid/alkali/acid	-24.6	5 830±30	6 732–6 554	6 647	
	8.7	331457	Bulk organic fraction: acid washes	-25.7	6 200±30	7 237–7 216, 7 209–7 199, 7 179–7 000	7 088	213
		329642	Peat fraction: acid/alkali/acid	-24.3	6 030±40	6 981–6 778, 6 763–6 755	6 875	
	9.16	331458	Bulk organic fraction: acid washes	-26.2	7 350±40	8 305–8 241, 8 217–8 029	8 162	1 045
		329645	Peat fraction: acid/alkali/acid	-27.4	6 220±40	7 250–7 140, 7 133–7 006	7 117	
	11.39	331455	Bulk organic fraction: acid washes	-26.5	7 210±40	8 158–8 085, 8 071–7 955	8 016	161
		329640	Peat fraction: acid/alkali/acid	-25.3	7 010±30	7 935–7 786, 7 771–7 763	7 855	
	13.05	331459	Bulk organic fraction: acid washes	-22.4	7 480±40	8 377–8 199	8 305	303
		329646	Peat fraction: acid/alkali/acid	-25.1	7 200±30	8 151–8 143, 8 128–8 122, 8 108–8 092, 8 057–7 952	8 002	
QX03	8.63	355245	Bulk organic fraction: acid washes	-25.8	7 480±40	8 377–8 199	8 305	955
		353798	Peat fraction: acid/alkali/acid	-26.7	6 410±40	7 420–7 271	7 350	
	9.6	355246	Bulk organic fraction: acid washes	-26.9	7 230±40	8 159–7 970	8 043	481
		353800	Peat fraction: acid/alkali/acid	-28.2	6 690±40	7 622–7 478	7 562	
	12.4	355247	Bulk organic fraction: acid washes	-23.2	7 570±40	8 429–8 325	8 385	288
		353802	Peat fraction: acid/alkali/acid	-28.3	7 280±40	8 174–8 013	8 097	
QX02	7.27	332793	Bulk organic fraction: acid washes	-27.0	6 910±40	7 832–7 671	7 739	456
		333329	Peat fraction: acid/alkali/acid	-25.7	6 350±30	7 413–7 390, 7 373–7 356, 7 331–7 240, 7 218–7 176	7 283	
	8.98	332794	Bulk organic fraction: acid washes	-26.5	7 130±40	8 019–7 922, 7 900–7 865	7 959	465
		333330	Peat fraction: acid/alkali/acid	-26.3	6 600±30	7 564–7 532, 7 522–7 434	7 494	
	10.97	332795	Bulk organic fraction: acid washes	-25.6	7 370±40	8 320–8 151, 8 143–8 129, 8 123–8 047	8 193	326
		333331	Peat fraction: acid/alkali/acid	-27.2	7 020±30	7 934–7 792	7 867	
	11.9	332796	Bulk organic fraction: acid washes	-26.3	8 130±40	9 245–9 216, 9 208–9 173, 9 139–8 996	9 069	1 096
		333332	Peat fraction: acid/alkali/acid	-26.6	7 150±40	8 029–7 927, 7 894–7 872	7 973	
	12.42	332797	Bulk organic fraction: acid washes	-25.5	7 470±40	8 372–8 196	8 291	325
		333333	Peat fraction: acid/alkali/acid	-26.3	7 140±40	8 023–7 925, 7 897–7 869	7 966	
ZW15	12.6	355822	Bulk organic fraction: acid washes	-22.5	8 030±40	9 024–8 760, 8 732–8 729	8 899	628
		356208	Peat fraction: acid/alkali/acid	-25.0	7 450±40	8 358–8 186	8 271	
	13.5	355823	Bulk organic fraction: acid washes	-24.5	8 570±40	9 597–9 484	9 537	1 197
		356209	Peat fraction: acid/alkali/acid	-25.5	7 640±40	8 537–8 529, 8 521–8 381	8 430	
	14.17	355826	Bulk organic fraction: acid washes	-21.7	12 700±50	15 303–14 894	15 132	6 634
		356211	Peat fraction: acid/alkali/acid	-26.4	7 720±40	8 581–8 423	8 498	
	15.05	355825	Bulk organic fraction: acid washes	-21.6	12 740±60	15 383–14 932	15 180	6 702
		356210	Peat fraction: acid/alkali/acid	-25.8	7 690±40	8 551–8 405	8 478	
Q7	4.32	358053	Bulk organic fraction: acid washes	-23.5	4 360±30	5 034–5 013, 4 977–4 853	4 922	1 172
		357147	Peat fraction: acid/alkali/acid	-26.1	3 470±30	3 833–3 683, 3 666–3 643	3 750	
	17.2	358055	Bulk organic fraction: acid washes	-19.2	8 280±40	9 417–9 133	9 287	419
		357153	Peat fraction: acid/alkali/acid	-28.0	7 990±40	9 005–8 705, 8 666–8 662	8 868	

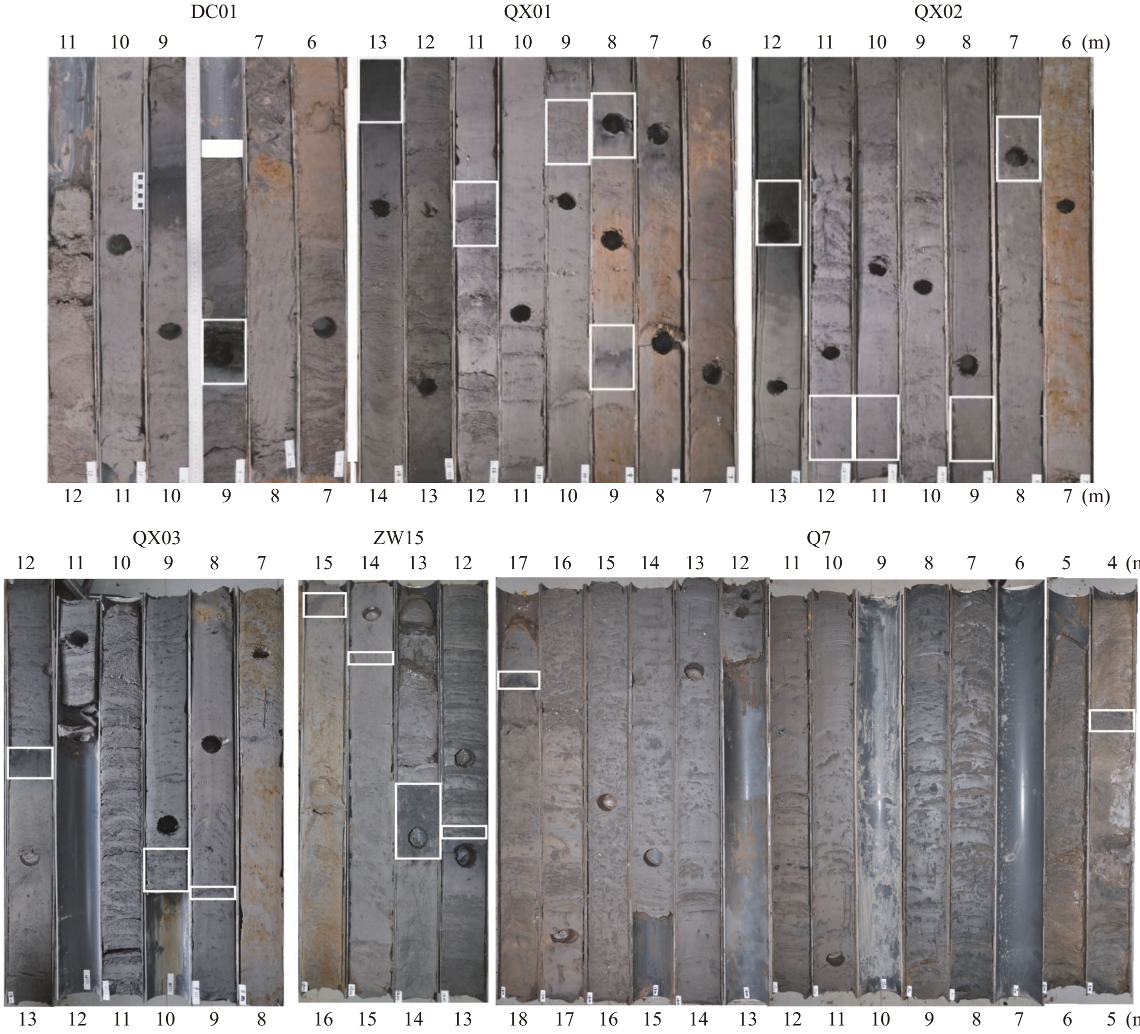

Fig.2 Peat layers in boreholes, white box is the peat layers have been sampled for AMS ^{14}C dating

Only 1–2 cm thick samples were collected in white box.

top layer, which is 7 690±40 → 7 720±40 → 7 640±40 → 7 450±40 yrs BP. Corresponding organic fractions give a wholly continuous age without disturbation, which is 12 740±60 → 12 700±50 → 8 570±40 → 8 030±40 yrs BP.

For borehole Q7, peat gives a continuous age without disturbation from bottom to top layer, which is 7 990±40 → 3 470±30 yrs BP. Corresponding organic fractions give a wholly continuous age without disturbation, which is 8 280±40 → 4 360±30 yrs BP.

5 DISCUSSION

Figure 3 shows that the ages of organic sediment fraction are disturbed with depth and their curves (the black line in Fig.3) based on sedimentary process is completely different compared with the curve of corresponding peat fraction (the red line in Fig.3) in the study boreholes except DC01. And the corresponding peat fraction usually gives a more stable age based on sedimentary processes and they also all showing the same age trend with depth (the red line in Fig.3). Further, the sedimentation rates show a decrease after 7 000 yrs BP based on the liner regression of the age and depth (Fig.3).

On the other hand, the ages given by organic sediment fraction are older than age given by corresponding peat fraction of boreholes QX01, QX03, QX02, ZW15 and Q7 except DC01 (Table 1 and Fig.3).

Only 1 bulk peat sample was collected from borehole DC01, and the ages given by organic sediment fraction and corresponding peat fraction in this layer are nearly the same. This layer was very pure peat, and nearly no muddy or sandy sediments. Diatom identification shows that this peat layer is deposited in fresh water swamp environment. From Fig.2, we can find that this peat layer that were found

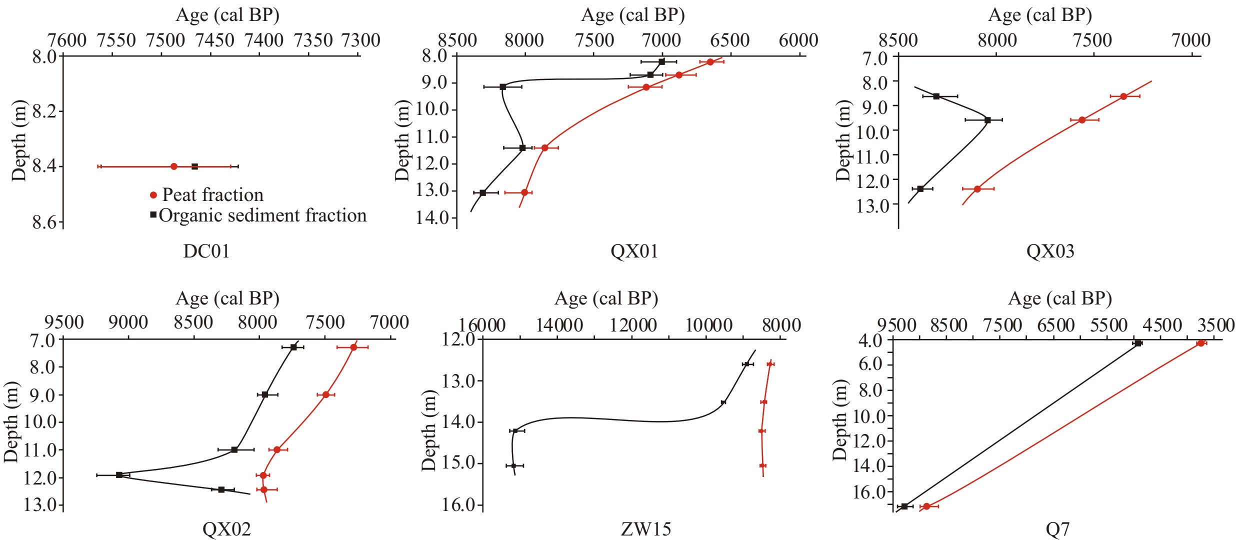

Fig.3 The calibrated ages of the two fractions for the study boreholes

Ages given by two fractions of peats for the study boreholes.

in the sediments grew in place on the surface of the sediment and then died and were incorporated into the sediment at the time of burial, so the peat data should be the most reliable. The organic sediment fraction gives the same age with peat in this layer, which means that the organic sediment fraction also gives a reliable age. Moreover, the borehole DC01 was 80 km away from modern coastline, which located on the land side of the boundary of the Holocene marine transgression maximum without marine influence.

In all of these cases the organic sediment fraction is yielding older ages (by about 161–6 702 years) than the peat fraction in the marine influence boreholes QX01, QX03, QX02, ZW15 and Q7. It is different results from general knowledge. Typically if the organic sediment fraction does not yield a result that is the same as the plant, it will yield a result that is somewhat more recent, due to the influences of mobilized dissolved organic carbon, in particular humic acids (typically from overlying younger sediments) and fulvic acids that can move down through stratigraphic profile or that are brought in due to the decomposition of plant matter or root exudation (Brock et al., 2011), groundwater flow (Waddington and Roulet, 1997). Moreover, Wüst et al. (2008) considers that fine-grained fractions (e.g. <100 μm) contain more highly degraded organic matter and Nilsson et al. (2001) thinks that it would be likely to get a young date.

There are two possible reasons for the organic sediments yield older ages than the peat fraction. 1) The intrusion of plant remains. Because of erosion or long periods of insufficient soil development, the plant grew into the older sediment and the intrusion happened. 2) Some or all of its carbon were got from an older source during the sediments' formation. For example, the reworking or redeposition of already deposited sediment from upslope by the mass movements, flooding or other physical processes.

In this paper, we suggest that the second possible reasons lead organic sediments yield older ages. Although the humic and fulvic acids, formed during humification, are the two important parts of the organic sediments and the humin may be most representative of the original plant material, it may still be contaminated with in-washed or intrusive carbon (Brock et al., 2011). Diatom and foraminifera identification on the depth of the age measured sediments (Table 1) for the five boreholes (QX01, QX02, QX03, ZW15 and Q7) are lacustrine or salt marsh deposition with marine influences, which means that they are deposited under water, and the sea water influence should be the main reason. The organic sediments were getting some or all of its carbon from older source during the marine transgression. Moreover, Compared with the boreholes QX01, QX03, QX02, ZW15 and Q7, the age distance between the organic sediment fraction and the corresponding peat fraction in the peat layers of these boreholes are getting bigger from landward to seaward (Fig.3). The boreholes closed to modern coast line were influenced stronger by the sea water than the boreholes closed to the landward during Holocene marine transgression maximum. And the

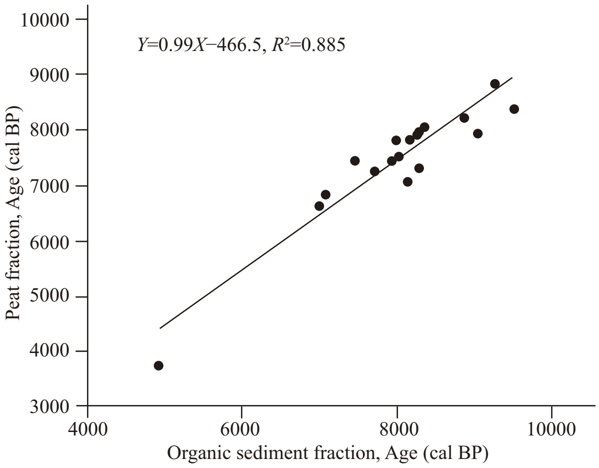

Fig.4 linear fit of the ages between the organic sediment fraction and peat fraction

marine influence becomes stronger to the seaward.

Southon et al. (2002) gave a value of -178±50 years as the marine reservoir age correction (ΔR) in Bohai Sea for the calibration of marine shells ^{14}C data (Reimer et al., 2013). Our study show that marine influence was a factor for the bulk organic sediment fractions of the marine peat layers on the west coast of Bohai Bay, and the effect became stronger to the seaward. Therefore, the marine influence should be considered for the marine influence organic sediment.

Further, we made a linear fit of the 18 group dating results of the organic sediment fraction and peat fraction after removing 2 group extreme values (Beta 355826 and 356211, Beta 355825 and 356210) (Fig.4). It indicated that the ages between the organic sediment fraction and the corresponding peat fraction are positive correlation and the correlation coefficient is 0.885. Then a formula as y=0.99x−466.5 was got and we propose it as a preliminary local experience formula for correcting the marine influenced organic sediment ages within the conventional ages between 4 000 to 9 000 yrs BP.

In general the ages of peat fractions are usually the most reliable because they typically represent a more unique event in time. In other words, the plants were relatively short lived when compared to the time it may have taken for the sediment to form. However when sediments do not contain extractable peat fractions, the ages of the organic sediment fractions usually get old ages and it should be considered the marine influence after their calibration in the marine influence peat layer.

6 CONCLUSION

(1) Compared with age given by organic sediment fraction, corresponding peat fraction usually gives a more stable age based on sedimentary processes and they also all showing the same age trend with depth. The sedimentation rates show a decrease after 7 000 yrs BP based on the liner regression of the age and depth.

(2) The dating results of organic sediment fraction show 161−6 702 years older than corresponding peat fraction, which could possibly be due to marine influence. Based on the correlation analysis of the dating results, we suggest a local experience formula as y=0.99x−466.5 for correcting the marine influenced organic sediment ages within the conventional ages between 4 000 to 9 000 yrs BP, which give a shed light to help improve the bulk organic sediments dating in these cores.

7 DATA AVAILABILITY STATEMENT

The datasets used and analyzed in the current study are available from the corresponding author on reasonable request.

8 ACKNOWLEDGEMENT

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