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Relocation of the Yellow River Estuary in 1855 AD Recorded in the Sediment Core from the Northern Yellow Sea

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Abstract Relocation of the Yellow River estuary has significant impacts on not only terrestrial environment and human activities, but also sedimentary and ecological environments in coastal seas. The responses of regional geochemical characteristics to the relocation event, however, have not been well studied. In the present study, we performed detailed geochemical elemental analyses of a sediment core from the northern Yellow Sea and studied their geochemical responses to the 1855 AD relocation of the Yellow River estuary. The results show that TOC/TN, Co/Al_2O_3, Cr/Al_2O_3, Ni/Al_2O_3 and Se/Al_2O_3 ratios all decreased abruptly after 1855 AD, and similar decreases are observed in the sediments of the mud area southwest off the Cheju Island. These abrupt changes are very likely caused by the changes in source materials due to the relocation of the Yellow River estuary from the southern Yellow Sea to the Bohai Sea, which the corresponding decreasing trends caused by the changes in main source materials from those transported by the Liaohe River, the Haihe River and the Luanhe River to those by the Yellow River. Because the events have precise ages recorded in historical archives, these obvious changes in elemental geochemistry of sediments can be used to calibrate age models of related coastal sea sediments.

Key words relocation of the Yellow River estuary; muddy sediments; northern Yellow Sea; elemental geochemistry

1 Introduction

Relocations of the Yellow River estuary are significant environment events; they affect not only human activities in the lower valley of the Yellow River, but also coastal sedimentary characteristics and ecological environment. Thus analysis of the responses of coastal sedimentary characteristics to the relocation of the Yellow River estuary is important for ecological study of coastal seas.

Both historical archives and sediments have been used to study relocations of the Yellow River. The earliest record of the Yellow River channel in historical archives was about the Yu River channel before 602 BC; after that the Yellow River channel changed frequently. There are 26 large relocation events in history, including 7 very important ones (Chen, 2001). The Yellow River estuary moved from the Bohai Sea to the southern Yellow Sea at 1128 AD, and moved back to the Bohai Sea at 1855 AD (Chen, 2001). Earlier studies on sediments from the Bohai Sea (Qiao *et al*., 2011), such as those from the mud area southwest off the Cheju Island (Yang *et al*., 2009) and the northern Yellow Sea (Sun *et al*., 2012), have all detected the 1855 AD relocation of the Yellow River estuary. Among these studies, only the sediments in the mud area southwest off the Cheju Island have been analyzed (Yang *et al*., 2009).

The northern Yellow Sea Mud (NYSM) is located in the east of the Bohai Bay. Materials in the NYSM are mainly from the Yellow River and transported across the Bohai Bay along the Shandong Peninsula. Sediments in this area are directly influenced by the runoff of the Yellow River (Yang and Liu, 2007) in modern times. However, the materials from the Yellow River could not reach this area when the Yellow River discharged into the southern Yellow Sea. Thus the NYSM is an ideal region for studying the relocation of the Yellow River estuary.

In the present study, we measured grain size and element concentrations of a sediment core from the NYSM, studied the 1855 AD relocation of the Yellow River estuary as recorded in proxies, and investigated the responses of elemental geochemical characteristics to the event.

2 Materials and Methods

In 2009, we collected a 34-cm-long sediment core from the NYSM area at Station 38002 (122˚30.21´E, 37˚59.92´N, water depth 49.2 m; Fig.1) using a box- corer during 'The Offshore Sea Open Research Cruise (Autumn)' aboard R/V *Kexue 1* of Institute of Oceanology,

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Chinese Academy of Sciences. The sediment core was divided at 0.5 cm interval into 68 sub-samples.

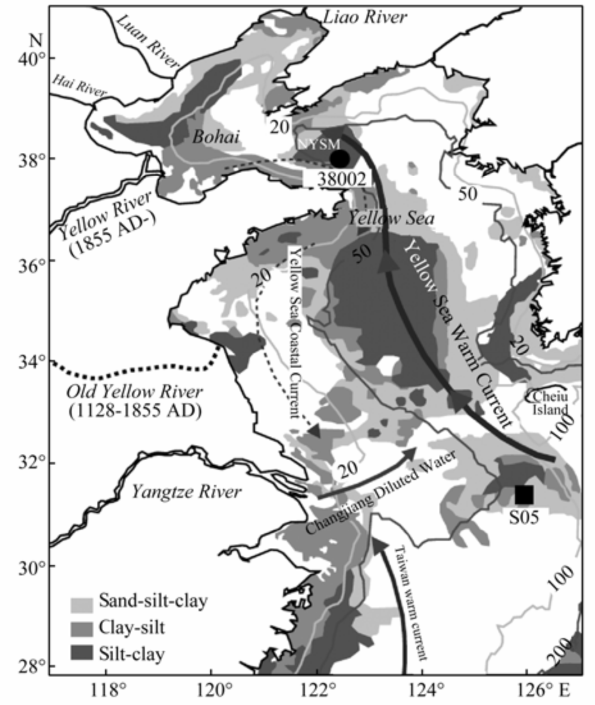

Fig.1 Location of the sampling site (map is modified from Li *et al*., 2005; Liu *et al*., 2007). Topographic lines are shown in light grey, mud areas are shown in dark grey, and coastal currents are marked by dashed lines and arrows.

Radioactivity was measured by a germanium detector manufactured by AMETEK Company at the Institute of Polar Environment, USTC, Hefei, China. The samples were dried to constant weight at a temperature of 50℃, homogenized using a mortar and pestle, and passed through a 120-mesh sieve. Samples (5–10 g) were then packed into standard counting geometries for gamma spectrometry and sealed and stored for about one week to allow radioactive equilibration between ^{226}Ra and its daughter product ^{214}Pb. Spectra were continuously measured for 24 h to obtain enough counts. The resulting spectrum files showed the 210Pb activity with a peak at 46.5 keV.

For pre-treatment of samples for grain size analysis, 10−20 mL H_2O_2 solution (30%) was added to remove organic matter at 150℃. Samples were subsequently bathed in 10 mL HCl solution (10%) for 48 h to remove calcareous cement and shell materials. All samples were fully desalted and dispersed by adding 10 mL $(NaPO_3)_6$ (10%) and by ultrasonic treatment for 10 min before measurement. Sample grain size was measured on Mastersizer 2000 (Malvern Instruments) at the Lab of Soil and Environmental Changes, Taishan University, China. The mea- surement range of the instrument is 0.02−2000 μm, with resolution 0.01 Φ and repeated measurement error less than 2%.

Total nitrogen content was measured on Vario EL III (Elementar Company) with an error less than 1%. The chemical volumetric method was used to measure TOC content with a duplicate error of 5% (Loring and Rantala, 1992). Concentrations of Co, Cr and Ni elements were digested by multi-acid treatments with $HF/HClO_4$ in a polyfluortetraethylene crucible with electric heating (about 250℃), and determined using atomic absorption spectrophotometry (AAS) (Model NOVAA400, Analytik Jena AG, Germany). Concentration of Sb was determined with Ordinal Interaction Two-pass Atomic Fluorescence Spectrophotometer (AFS-930, Beijing Jitian Instrument Co., China). To validate the procedure, national standards GBW07403, GBW07404, GBW07603, GBW07605, and GBW07106 were used as quality control with a duplicate error of 5%.

3 Results and Discussion

The chronology of the sediment core 38002 was determined by the ^{210}Pb–^{137}Cs dating method (Fig.2), using a Constant Initial Concentration (CIC) computer model (Appleby, 2001). The excess ^{210}Pb activity showed a simple exponential relationship with depth (Fig.2). From the ^{210}Pb profile, the age of the ^{137}Cs peak at 8.5 cm was determined to be 1961 AD, very close to the presumed ^{137}Cs

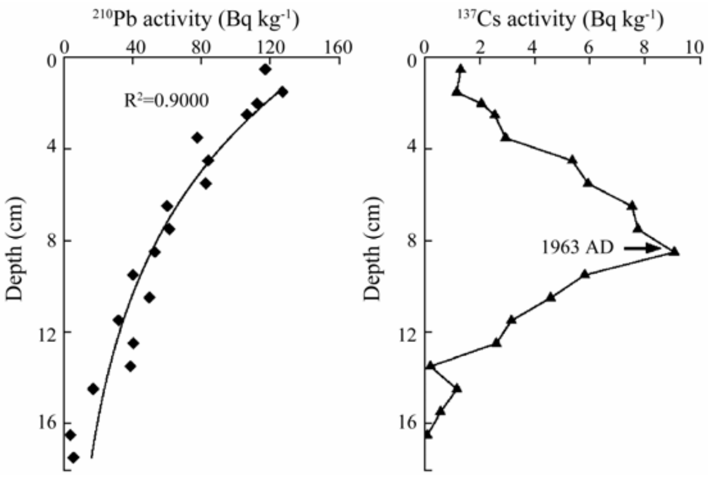

Fig.2 Activity profiles of ^{210}Pb and ^{137}Cs for the sediment core 38002 (data from Sun *et al*., 2012 and Zhou *et al*., 2012).

peak age of 1963 AD. This correspondence validates the accuracy of the ^{210}Pb dating. For this reason we use ^{210}Pb as the primary age control on the core. From ^{210}Pb data the average sedimentation rate was calculated to be 0.13 cm yr^{-1}, consistent with earlier results (Li *et al*., 2002; Qi *et al*., 2004). The time period recorded by the core is about 254 yr (1755–2009 AD), as estimated by extrapolation of this average sedimentation rate.

Median grain size of the sediment core 38002 (Fig.3) showed no significant changes in trends, with small oscillations between 1750 and 1830 AD. From 1830 to 1900 AD, the median grain size increased gradually with no abrupt change; but after 1900 AD it showed large amplitude of oscillation. There's no abrupt change in median grain size around 1855 AD when the Yellow River estuary relocated, indicating that the proxy is not sensitive to the event. Before 1855 AD, other rivers, such as the Haihe River and the Luanhe River that are located in the same climate zone as the Yellow River, could transport materials into the northern Yellow Sea. Because sedimentary characteristics of sediments are mainly controlled by the climate factors (monsoon precipitation), the median grain size could not be significantly influenced by the relocation events as indicated by Zhou *et al*. (2012).

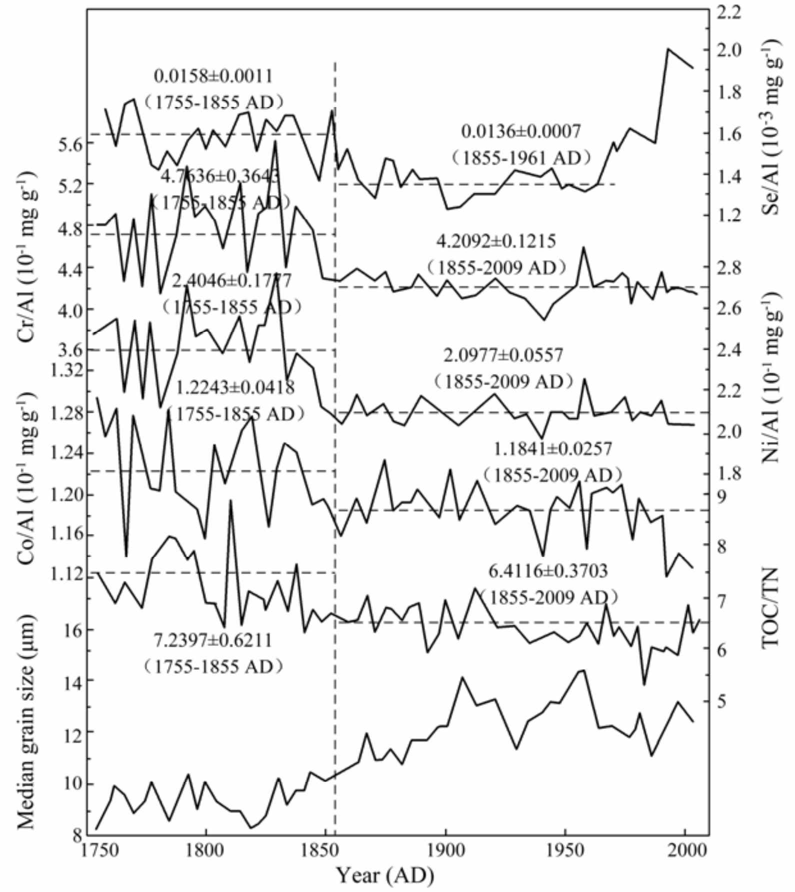

Fig.3 Time series of median grain size (data from Sun *et al*., 2012; Zhou *et al*., 2012), TOC/TN, Co/Al, Ni/Al, Cr/Al and Se/Al for the sediment core 38002. Data in the figure show the mean and standard deviation of the values of the proxies before and after 1855 AD.

Unlike median grain size, geochemical proxies, including TOC/TN, Co/Al, Ni/Al, Cr/Al and Se/Al ratios, all showed abruptly decreases around 1855 AD (Fig.3), and they recorded the 1855 AD relocation of the Yellow River estuary well.

Generally, TOC/TN ratio of organic materials originated from aquatic plants (<10) is lower than that from terrestrial plants (14−30), and TOC/TN ratio is usually used to study changes in source materials, with high value indicating terrestrial sources, and low value indicating marine sources (*e.g*. Zhu *et al*., 2002; Zhang *et al*., 2009). Sediments in the NYSM were mainly from materials transported by the Yellow River after 1855 AD, but by other rivers such as Haihe River and Luanhe River when the Yellow River discharged into the southern Yellow Sea between 1128 and 1855 AD. Large amounts of materials from the Yellow River would significantly increase terrestrial materials in sediments of the NYSM and thus increase the TOC/TN ratio after 1855 AD. Actually, however, the TOC/TN ratio decreased abruptly after 1855 AD (Fig.3). Earlier study (Zhang and Liu, 2008) found that TOC/TN ratio of loess is between 3 and 11, substantially lower than those of other terrestrial materials. Thus, import of more materials from the Loess Plateau by the Yellow River after the relocation of the Yellow River estuary reduced TOC/TN ratio in sediments of the NYSM.

The abrupt changes in elemental geochemistry of the sediment core around 1855 AD might also be attributed to the changes in source materials. We compared Co/Al_2O_3, Cr/Al_2O_3, Ni/Al_2O_3 and Se/Al_2O_3 ratios in loess with the averaged ones of the soils in Liaoning Province of the Liaohe River valley and in Hebei Province and Beijing and Tianjin regions of the Haihe and Luanhe River valleys (Wei *et al*., 1990). The element ratios in loess are lower than those in soils from other regions. Because the sediment source materials changed from those transported by the Liaohe River, the Haihe River and the Luanhe River before 1855 AD to loess transported by the Yellow River after 1855 AD, the corresponding decreases in element ratios are most likely caused by relocation of the Yellow River estuary.

Geochemical characteristics of sediments in the NYSM and those in the mud area southwest off the Cheju Island (Fig.4) showed similar decreasing trends around 1855 AD, indicating similar responses of sediments in both regions to the 1855 AD relocation of the Yellow River estuary. Because the relocation event has its precise age recorded in historical archives, the corresponding changes in geochemical characteristics can be used to calibrate the age model of sediment cores in the related coastal seas.

Table 1 Comparison of Co/Al_2O_3, Cr/Al_2O_3, Ni/Al_2O_3 and Se/Al_2O_3 ratios between loess and soils in provinces around the Liaohe River, the Haihe River and the Luanhe River valleys (data of loess from Tian *et al*., 1991, other data from Wei *et al*., 1990)

Regions	Element ratio (10^{-1} mg g^{-1})			
	Co/Al_2O_3	Cr/Al_2O_3	Ni/Al_2O_3	Se/Al_2O_3
Liaoning and Hebei Provinces, Beijing and Tianjin regions	1.30	5.57	2.47	1.18
Loess Plateau	0.94	5.10	2.35	0.35

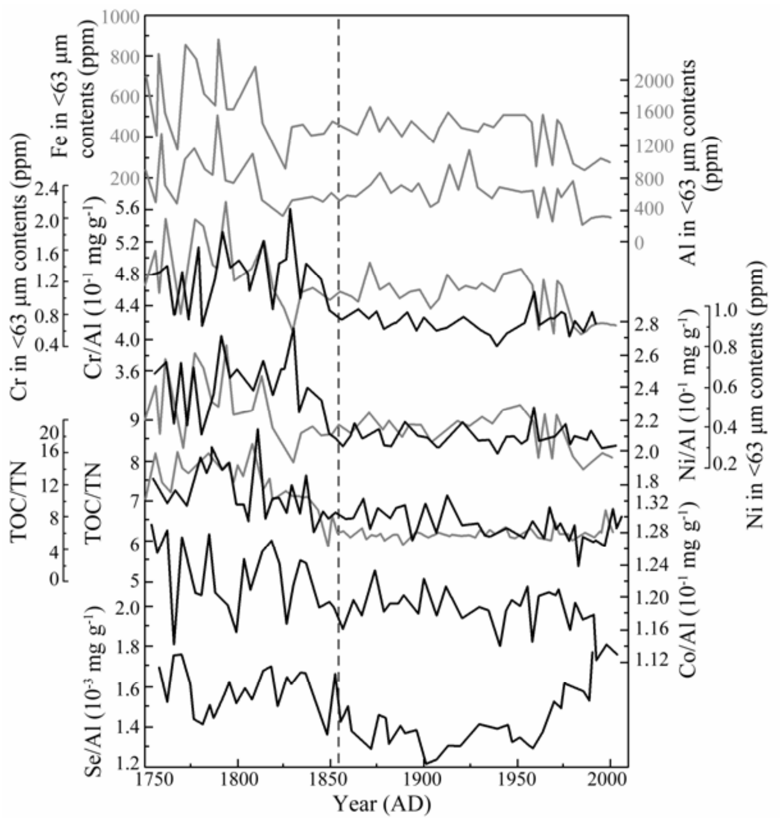

Fig.4 Comparison of proxies for sediment core 38002 with those for core S05 (data from Yang *et al*., 2009).

4 Conclusions

In summary, we studied the changes in TOC/TN, Co/Al_2O_3, Cr/Al_2O_3, Ni/Al_2O_3 and Se/Al_2O_3 ratios of sediments in the NYSM in response to the 1855 AD relocation of the Yellow River estuary. These proxies all decreased abruptly around 1855 AD when the Yellow River estuary relocated from the southern Yellow Sea to the Bohai Sea. These decreasing trends are most likely caused by the changes in main source materials from those transported by the Liaohe River, the Haihe River and the Luanhe River to those by the Yellow River. The consistence between geochemical characteristics of the sediments in the NYSM and the mud area southwest off the Cheju Island suggests the significant influences of the relocation event on the sedimentary environment of the Yellow Sea.

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