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Evidence for paleoclimate changes from lignin records of sediment core A02 in the southern Yellow Sea since ~9.5 cal. kyr B.P.

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ABSTRACT

Sediment core A02 collected from the central Yellow Sea mud (CYSM) was analyzed for various lignin parameters to provide evidence for the paleoclimate changes in the southern Yellow Sea (SYS) area during the Holocene. The results showed that the variations of various lignin parameters were dominated by the hydrodynamic sorting process driven by climate factors, and in turn lignin records can well reflect paleoclimate changes during the Holocene. The paleovegetation of the Yellow River basin was dominated by nonwoody angiosperms, and the terrestrial organic matter in core A02 was highly degraded and mainly came from peat and surface soils. Compared with climate records in previous studies, we found that terrestrial organic matter indicator Σ8, marine organic matter indicator P phenols and vegetation parameters S/V, C/V ratios had the similar variation trends with the El Niño-Southern Oscillation (ENSO) on the millennial time scale and correlated well with the Bond events (0 to 6) and the East Asian Winter Monsoon (EAWM) on the multidecadal to centennial time scale. ENSO events dominated the long-term trends of the biomarkers in the SYS during the Holocene while EAWM for the shorter time scale. Lignin records of core A02 responded not only to the regional climatic factors such as the EAWM but also to the global climatic factors such as Bond events and ENSO. In addition to the global cold climate events, it also recorded other regional cold events (at around 3.7 cal. kyr B.P., 6.5 cal. kyr B.P. and 7.0 cal. kyr B.P.) and coincided well with previous related records in the East Asian. These proved that the paleoclimate in SYS area was controlled by both regional and global climatic factors.

1. Introduction

Studies of paleoclimate changes are important because they can provide a wealth of information to help us to master the mechanism of current climate changes and to be able to predict the future climate changes. Continuously deposited marine sediments whose age can be relatively easily determined are good archives of past climate change (Moreno and Canals, 2004). In fact, most organic matter is deposited and buried in continental margins and not in the pelagic ocean (Berner, 1992; Cathalot et al., 2013). The organic matter in coastal areas especially the fine-grained component is transported to the offshore area mainly via the hydrodynamic sorting process during the resuspension (Mitra et al., 2000; Kuzyk et al., 2008). This process is related to the ocean circulation and climate factors (Bi et al., 2011; Hu B.Q. et al., 2012; Zhou et al., 2015). The Yellow Sea (YS, Fig. 1) is a semi-enclosed, western Pacific marginal sea, located between the east coast of China and the west coast of the Korean peninsula (Takahashi et al., 1995; Lim et al., 2006). It is strongly influenced by the El Niño-Southern Oscillation (ENSO) (Wei et al., 2010) and the East Asian Monsoon (EAM) which includes the East Asian Summer Monsoon (EASM) and the East Asian Winter Monsoon (EAWM) (Badejo et al., 2016). The YS circulation system mainly consists of the Yellow Sea Warm Current (YSWC) flowing northward from the area just west of Cheju Island, Korea, the Yellow Sea Coastal Current (YSCC) and the Korean Coastal Current (KCC) (Fig. 1) (Yuan et al., 2008; Moon et al., 2009; Jin et al., 2014). The Yellow Sea Cold Water Mass (YSCWM), which is prominent in summer and autumn, is also a characteristic feature of the YS (Li et al., 2006; Moon et al., 2009). Under such hydrological and climatic conditions, the sediments of the central Yellow Sea mud (CYSM, Fig. 1) are supplied by the suspended sediments delivered with the climate-forced (especially the EAWM) currents in winter, which is summarized as "storing in summer, transporting in winter". The transport and

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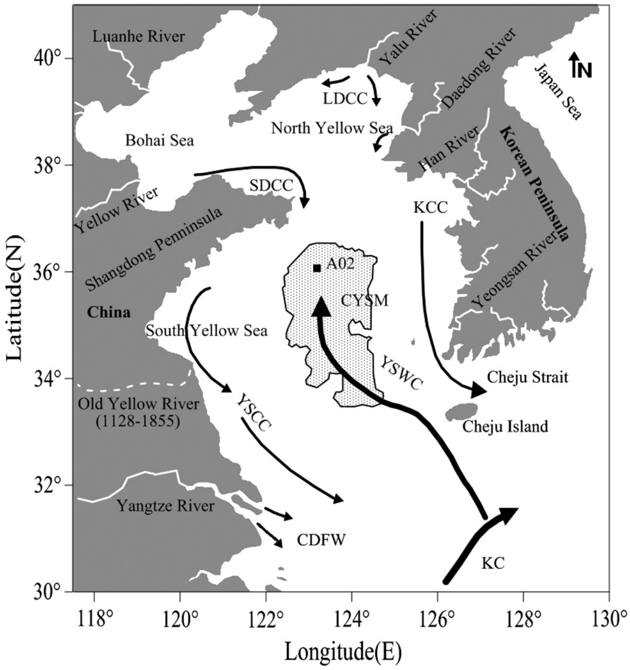

Fig. 1. Map showing the study area, location of core A02 (black square) and surface current system (black arrows) around the area, modified after Mei et al. (2016). Gray shaded area indicates CYSM (central Yellow Sea mud). LDCC: Liaodong Coastal Current; SDCC: Shandong Coastal Current; YSCC: Yellow Sea Coastal Current; CDFW: Changjiang Diluted Freshwater; KC: Kuroshio Current; KCC: Korea Coastal Current; YSWC: Yellow Sea Warm Current.

deposition regime seems to remain relatively unchanged over the past 7 kyr (Hu B.Q. et al., 2012). Therefore, the CYSM in the southern Yellow Sea (SYS) formed by the combined effect of hydrodynamic factors (Zhou et al., 2015) provides desirable materials for high-resolution paleoclimate studies.

As a specific component of vascular plants, lignin is a useful tool to reconstruct the input, transport and deposition of terrestrial organic matter in coast and open seas or other environments (Bianchi et al., 1999; Benner and Opsahl, 2001; Dittmar et al., 2001; Kuzyk et al., 2008; Tareq et al., 2011). The hydrodynamic sorting process preferentially delivers the fine-grained sediments, which are lignin-poor and more degraded (Hedges et al., 1986; Tesi et al., 2008; Thevenot et al., 2010; Cathalot et al., 2013; Li et al., 2013), and carry more nonwoody angiosperm materials (Hu L.M. et al., 2012; Li et al., 2014; Kuzyk et al., 2008; Bianchi et al., 2011) than the coarse particles to the CYSM. And this sorting process is driven by climatic factors. Therefore, we can conclude that the content and composition of lignin in sediments are relevant with the hydrodynamic sorting process driven by climate factors, and we then consider that lignin record may in turn reflect the climate changes. There existed a variety of proxies for paleoclimate studies of the YS. For instance, sensitive grain size groups were used as a proxy to reconstruct the history of the EAWM during the last 7.2 kyr (Hu B.Q. et al., 2012), lipid biomarkers and the isotopic composition of organic matter used to understand the past changes in EAM climates (Badejo et al., 2016) and there were other proxies such as benthic foraminiferal assemblages (Kim and Kucera, 2000) and sporo-pollen assemblages et al. (Meng et al., 2004). Compared with these previous studies, our lignin proxy has clear time series and the sediment core A02 from the CYSM spans the past 9489 yr with a high resolution of approximately 31 yr cm^{-1} on average. Then we speculate that our lignin records can well reflect the Holocene paleoclimate on the basis of these previous studies.

In this paper, the lignin biomarkers were analyzed for the sediment core A02 form the CYSM. We first studied the concrete relationship between the hydrodynamic sorting process driven by climate and the variations of lignin records to make sure if the hydrodynamic sorting process is the dominated factor for the variations of lignin records. Then we analyzed lignin records combined with various climate records and other biomarkers records in order to confirm that lignin biomarkers can really effectively reconstruct the paleoclimate and clarify how the paleoclimate changed in the SYS during the Holocene. In addition, the vegetation types of the provenance region and degradation of terrestrial organic matter were also discussed.

2. Materials and methods

2.1. Sampling

The sediment core A02 (36°4.2′N, 123°11.4′E) was recovered from the CYSM (Fig. 1) by R/V Dong-Fang-Hong 2 in the spring of 2011. The water depth of this sediment core is 73.4 m and core length is 304 cm. The core was subsampled at 1 cm intervals to yield 279 core sediment samples (there is a fault at 41–60 cm in this sediment core) for lignin analysis. All of the subsamples were freeze-dried and ground to pass 80 mesh sieve before analysis.

2.2. Methods

2.2.1. CuO oxidation

Lignin phenols were analyzed using the alkaline CuO method (Hedges and Ertel, 1982; Goñi and Montgomery, 2000; Miltner and Emeis, 2000) as modified by Zhang et al. (2013). Briefly, about 1 g (containing 2–5 mg organic carbon) ground dry sediment was placed in a Teflon reaction vessel with 500 mg CuO, 50 mg $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. Then 2 mol/L NaOH was added to the vessel in a nitrogen filled glove box. The vessel was placed at 170 °C for 3 h and recovery surrogates (ethyl vanillin and trans-cinnamic acid) were added after the vessel cooling down under the running tap water. Next, the content of the vessel was transferred to the glass tubes and then centrifuged, washed, separated and acidified to a pH of 1 with concentrated HCl. The sample solution was extracted by Cleanert SPE column (500 mg, Agela Technologies) and eluted by ethyl acetate. The eluate was dried under a gentle stream of N_2 and was frozen at −20 °C until analysis. The sample was re-dissolved in acetonitrile and derivatized with bis-trimethylsilyl-trifluoroacetamide (BSTFA) mixed with 1% trimethylchlorosilane (TMCS) before injection. GC analysis was carried out using an Agilent 6890 series Gas Chromatography coupled with Flame Ionization Detector (GC/FID) and a DB-1 chromatography column (30 m × 0.25 mm i.d. × 0.25 μm film thickness). The injector and detector temperatures were set to 300 °C and the oven temperature was programmed from 100 °C to 290 °C at 4 °C min^{-1}, holding for 10 min. The identification of the individual compounds was based on the chromatographic retention time of the standard compounds. Triisopropylbenzene was used as the internal standard and the seven-point standard curves were made for the quantification of the recovery surrogates and individual compounds, following the method described previously by Zhang et al. (2013).

2.2.2. Lignin CuO oxidation parameters

In this paper, lignin-phenols used as molecular indicators included three vanillyl phenols (V; vanillin (Vl), acetovanillone (Vn) and vanillic acid (Vd)), three syringyl phenols (S; syringaldehyde (Sl), acetosyringone (Sn) and syringic acid (Sd)), two cinnamyl phenols (C; *p*-coumaric acid (pCd) and ferulic acid (Fd)). Other compounds derived from the CuO oxidation used as molecular indicators included three *p*-hydroxybenzenes (P; *p*-hydroxybenzaldehyde (Pl), *p*-hydroxyacetophenone (Pon) and *p*-hydroxybenzoic acid (Pd)) and 3,5-dihydroxybenzoic acid (3,5-Bd) (Hedges and Mann, 1979; Goñi and Hedges, 1995).

Lignin parameters derived from these indicators are as follows. Σ8 (mg/10gds) is the total concentration of eight lignin phenols (C, S and V phenols) relative to 10 g dry sediment (ds) and is used as an indicator

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