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Response of carbon isotopic compositions of Early-Middle Permian coals in North China to palaeo-climate change

Dianshi Ding[a,b], Guijian Liu[a,b,*], Xiaohui Sun[a], Ruoyu Sun[c]

[a] CAS Key Laboratory of Crust-Mantle Materials and the Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China

[b] State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, The Chinese Academy of Sciences, Xi'an 710075, Shaanxi, China

[c] Institute of Surface-Earth System Science, Tianjin University, Tianjin 300350, China

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ABSTRACT

To investigate the magnitude to which the carbon isotopic ratio ($\delta^{13}C$) varies in coals in response to their contemporary terrestrial environment, the Early-Middle Permian Huainan coals (including coals from the Shanxi Formation, Lower Shihezi Formation and Upper Shihezi Formation) in North China were systematically sampled. A 2.5‰ variation range of $\delta^{13}C$ values (−25.15‰ to −22.65‰) was observed in Huainan coals, with an average value of −24.06‰. As coal diagenesis exerts little influence on carbon isotope fractionation, $\delta^{13}C$ values in coals were mainly imparted by those of coal-forming flora assemblages which were linked to the contemporary climate. The $\delta^{13}C$ values in coals from the Shanxi and Lower Shihezi Formations are variable, reflecting unstable climatic oscillations. Heavy carbon isotope is enriched in coals of the Capitanian Upper Shihezi Formation, implying a shift to high positive $\delta^{13}C$ values of coeval atmospheric CO_2. Notably, our study provides evidence of the Kamura event in the terrestrial environment for the first time.

1. Introduction

Geochemical and physical characteristics of coal deposits could provide important information concerning palaeo-environmental and palaeo-climatic changes that occurred between the initiation and termination of a coal seam. Among those, the stable carbon isotopic ratio ($\delta^{13}C$) of coals is a robust tracer to reflect local, regional and even global carbon cycle in the Earth's history (Jones et al., 1997; Lücke et al., 1999; Bechtel et al., 2003a; Chen et al., 2014). The $\delta^{13}C$ values of coals have been successfully applied to the study of the terrestrial environment during the Cenozoic (Jones et al., 1997; Lücke et al., 1999; Bechtel et al., 2007; Holdgate et al., 2007, 2009; Chen et al., 2014). The climatic parameters derived from coal $\delta^{13}C$ values agree well with those of co-located other geological records. However, there are only limited carbon-isotopic data for Permian coals (Faure et al., 1995; Singh et al., 2012).

During the Permian, North China had a prosperous biological community and a preferably depositional environment for coal accumulation due to the wide expansion of C3 plants. Therefore, multiple layers of coal seams with different thickness were deposited. This paper reports $\delta^{13}C$ values for Early-Middle Permian coals in the Huainan coalfield, eastern China, and highlights their implication for palaeo-climatic change.

2. Geological setting

The Huainan coalfield is located in northern Anhui province, China. The coalfield has an elongated outline with a length of 180 km and a width of 15–25 km, and covers an area of 3200 km^2 and contains coal reserves of approximately 44,000 Mt (Sun et al., 2010). At present, there are sixteen mines under construction or production (Fig. 1).

2.1. Coal-bearing strata

Within the coalfield, multiple coal seams were accumulated during the Permian, comprising the Shanxi Formation (52–88 m), the Lower Shihezi Formation (106–265 m) and the Upper Shihezi Formation (316–566 m). Along the sequence upward, the coal seams are numbered in an ascending order. Laterally, one seam could have sub-seams due to splitting and pinch-out. The detailed stratigraphic and lithological characteristics of the coal-bearing strata are shown in Fig. 2.

* Corresponding author at: CAS Key Laboratory of Crust-Mantle Materials and the Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China.

E-mail address: lgj@ustc.edu.cn (G. Liu).

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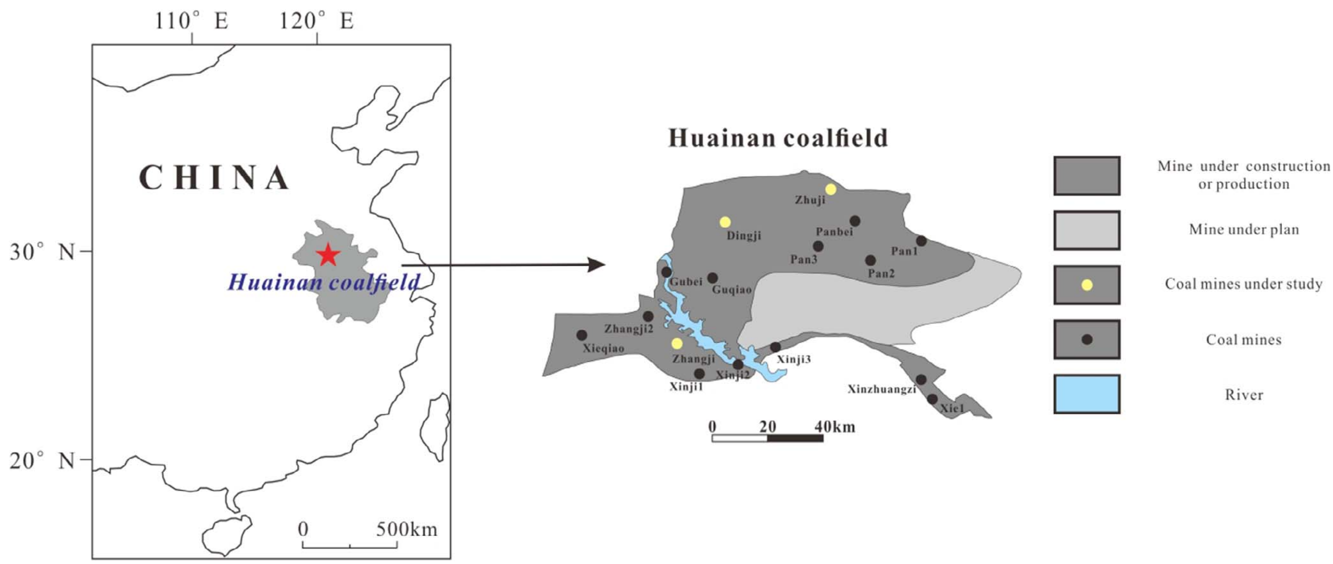

Fig. 1. Location map of the Huainan coalfield (modified from Sun et al. (2010)).

2.2. Age framework

The stratigraphic correlation of Permian terrestrial sequences in North China with the IUGS Global Chronostratigraphy is problematic due to lacking of high-resolution biostratigraphy and sedimentary ages. Here, we adopt a relatively accurate age framework presented by Wang (2010), which is constructed by compiling all available data for plant macrofossil assemblages and sporopollen assemblages, to discuss the palaeo-climatic changes during deposition of the studied Permian coals (Fig. 3).

3. Samples and methods

3.1. Sample collection

A total of 135 coal samples were sampled from three coal mines: Zhangji Mine (n = 39), Dingji Mine (n = 53) and Zhuji Mine (n = 43). These samples cover 15 coal seams (Nos. 1, 3, 4-1, 4-2, 5-1, 5-2, 6, 7-1, 7-2, 8-9, 11-1, 11-2, 13-1 and 13-2) in the Permian coal-bearing sequences of the Huainan coalfield. All these coal samples were sampled from non-magmatic intrusion areas to rule out magmatic influences. Each sample represents a mixture of up, middle and low benches of individual coal seams (Supplementary Table 1).

3.2. Preparation and analysis

The bulk coal samples were dried at room temperature and ground to pass a 120-mesh sieve to obtain homogeneous particles. High Temperature Burning Oxidation method was used for determination of organic carbon isotopic ratio of coals (Cao et al., 2005). Briefly, powder coal aliquots were firstly treated with excessive HCl (2M) for 24 h at room temperature to remove inorganic carbonate and soluble organic carbon, and then were washed to neutral with Millipore water before drying at 40 °C. An airtight silica tube containing approximately 0.3 g of prepared coal sample and copper oxide, copper and platinum wire was vacuumized and combusted for 4 h at 850 °C to produce CO_2 that was subsequently isolated and purified by an alcohol-liquid nitrogen cold trap under vacuum system. The trapped CO_2 was measured for $^{13}C/^{12}C$ value using an isotope ratio mass spectrometer (MAT-252 at Institute of Earth Environment, CAS, China), and the results are expressed in delta (δ) notation relative to the V-PDB standard:

$$\delta^{13}C(‰) = (Rsa/Rst-1) \times 1000$$

where Rsa is $^{13}C/^{12}C$ value of the measured coal sample, and Rst is $^{13}C/^{12}C$ value of the VPDB standard. All samples were measured in triplicate. International isotopic standards USGS24 (graphite, $\delta^{13}C = -16.049‰$) and LSVEC (lithium carbonate, $\delta^{13}C = -46.6‰$) were used to qualify the analytical uncertainty of $\delta^{13}C$ which is typically within ± 0.1‰.

4. Results and discussion

4.1. Carbon isotopic ratio of coals in the Huainan coalfield

The $\delta^{13}C$ of Huainan Permian coals exhibited a range from −25.15‰ to −22.65‰, with an average value of −24.06‰. The observed $\delta^{13}C$ values are generally comparable to those of coals deposited in other coal-forming periods. For example, the $\delta^{13}C$ values of Eocene-Miocene coals in southeast Australia ranged from −27.7‰ to −23.2‰ (Holdgate et al., 2009). In the upper Miocene lignite deposit, Austria, the $\delta^{13}C$ values of lignite varied from −27.2‰ to −24.6‰ (Bechtel et al., 2007). The Middle Miocene brown coals from Germany showed more depleted $\delta^{13}C$ values, ranging from −26.7‰ to −25.2‰ (Lücke et al., 1999). Recently, Singh et al. (2012) reported that the mean $\delta^{13}C$ value in Indian Permian coals was −22.58 ± 0.20‰. Van de Wetering et al. (2013) showed that $\delta^{13}C$ values in Australian coals ranged from −26.6‰ to −21.9‰ in the Late Permian, and from −25.2‰ and −20.9‰ in the Late Jurassic (Hentschel et al., 2016). Therefore, the $\delta^{13}C$ values of studied coals lied within the typical variation range for global coals (Suto and Kawashima, 2016).

4.2. Variations of carbon isotopic ratio among different mines

There was little difference in $\delta^{13}C$ among the investigated three mines. The mean $\delta^{13}C$ value in samples from the Zhangji Mine, Dingji Mine and Zhuji Mine were −23.97‰, −24.02‰ and −24.18‰, respectively (Supplementary Table 2). Specifically, for the individual coal seams, their $\delta^{13}C$ values in different mines were quite similar (Table 1 and Fig. 4). However, the coal sample number in different mines and each coal seam was not even allocated, due to the working difficulty during sample collection.

Slight difference in $\delta^{13}C$ was seen between the split coal seams. Table 1 and Fig. 4c shows $\delta^{13}C$ values in split coal seams 7-1 and 7-2 of the Lower Shihezi Formation from the three mines. For the 7-2 coal seam, $\delta^{13}C$ values of coals from the Zhangji Mine and Dingji Mine were slightly higher compared with the Zhuji Mine. In contrast, $\delta^{13}C$ value of