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Terrestrial *n*-alkanes and their carbon isotope records from the Hanon paleo-maar sediment, Jeju Island, Korea: Implications for paleoclimate and paleovegetation over the last 35 kyrs

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ABSTRACT

The carbon isotope of total carbon ($\delta^{13}C_{org}$), long-chain *n*-alkanes, and their compound-specific carbon isotope ratios ($\delta^{13}C_{ALK}$) were investigated in the Hanon paleo-maar sediment, Jeju Island of Korea to understand paleoclimate variabilities and their paleovegetation linkages. Based on the organic geochemical data (TOC (%), TN (%), and their $\delta^{13}C_{org}$ and $\delta^{15}N$), the core column stratigraphy was divided into three units, namely from the bottom to 14.5 ka (Unit I), from 14.5 ka to 3.0 ka (Unit II), and from 3.0 ka to the core top (Unit III), respectively. In particular, $\delta^{13}C_{org}$ showed marked fluctuation from −17.31‰ to −28.68‰, suggesting different organic carbon sources. A relatively narrow range of variation in $\delta^{13}C_{org}$ was observed in Unit III, and drastic changes in $\delta^{13}C_{org}$ were observed from Unit I to Unit II. This may indicate a predominance of C_4 plants in Unit I, and drastic changes from terrestrial C_4 to C_3 in Unit II and predominance of C_3 plants in Unit III. The distributions of *n*-alkane were characterized by a continuous predominance of odd-numbered *n*-alkanes, particularly nC_{29} and nC_{31}, and by high fluctuation of the total *n*-alkanes concentration. The average chain length (ACL), carbon preferences index (CPI), and paleoplant proxy (P*aq*) showed high fluctuation and glacial-interglacial variations with distinctive a high and low ratio at about 9.2 ka, corresponding to the switching points of $\delta^{13}C_{org}$ and a high concentration of *n*-alkane distribution. Individual *n*-alkane odd-numbered isotopes of $\delta^{13}C_{ALK}$ ranged between −11.80‰ in $\delta^{13n}C_{21}$ and -34.93‰ in $\delta^{13n}C_{31}$, suggesting different sources of *n*-alkanes. The distribution of *n*-alkanes and their individual $\delta^{13}C_{ALK}$, in particular $\delta^{13n}C_{21}$, support paleovegetation changes, and their time-dependent variations matched well with glacial-interglacial paleoclimate variations. Therefore, organic geochemical proxies recorded in Hanon paleo-maar sediment reflects paleoclimate variabilities as well as paleovegetation changes for the last 35 kyr in Jeju Island, Korea.

1. Introduction

Responses to climatic variation during glacial and interglacial periods are prominent characteristics that indicate the alternation of cold and warm climate conditions in the global climatic system (Alley et al., 2003; Wang et al., 2005; Lee et al., 2008; Li et al., 2013). In particular, millennial-scale cold and warm climatic signals have been clearly demonstrated not only in global areas (Lea et al., 2003; Sikes et al., 2009; Litwin et al., 2013; Jia et al., 2015) but also the East Asian area where monsoon climatic changes are prominent (An, 2000; Wang et al., 2001; Lim et al., 2005; Takahara et al., 2010; Nagashima et al., 2011; Park et al., 2014; Wang et al., 2014a,b). There have been numerous previous studies on these alternating paleoclimatic records evident in terrestrial, lacustrine and oceanic sediment (Wang et al., 2014a,b; Li et al., 2016). Indeed, previous studies have reconstructed past glacial-interglacial variations in East Asian monsoon records, and they have further demonstrated that these records are in synchroneity or anti-phase with global records (e.g., Tada et al., 1999; Wang et al., 2001; Yokoyama et al., 2006; Jia et al., 2015).

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As a powerful proxy, sedimentary *n*-alkanes of higher plant leaf-wax, have been used to reconstruct past variations in paleoclimatology, and paleovegetation records (Zhang et al., 2006; Litwin et al., 2013; Jia et al., 2015). In particular, higher plant leaf-wax can be easily transported over long distances, its content or accumulation indicates palcoclimatic variation (Ohkouch et al., 1997). For example, Yokoyama et al. (2006) clearly demonstrated that there was a high content of plant leaf-wax deposited during glacial periods and lower content during interglacial periods in sediment from the East Sea (Sea of Japan), and discussed strong transport intensity during glacial periods. Similarly, Yamada and Ishiwatari (1999) showed that long-chain *n*-alkanes and their compound-specific $\delta^{13}C_{ALK}$ are closely related to the glacial-interglacial cycle and suggested that the positive shift in $\delta^{13}C$ during around 10 ka BP can be attributed to either primary productivity on land or change vegetation in type.

The vegetation changes in certain region are strongly influenced by climate variations and topographic gradients, as many terrestrial plants are strongly linked to the temperature and humidity of specific environments. Many studies have shown that vegetation changes are directly associated with changes in local climatic conditions (Takahara et al., 2010; Lim et al., 2013; Li et al., 2016). This tight association between climatic and vegetation changes may have had a global effect (Litwin et al., 2013), and may have even had an impact on human life during the Anthropocene period (Alley et al., 2003). Therefore, paleo-vegetation changes have been tracked and interpreted in terms of paleoclimate variation using various organic proxies, such as a carbon isotope of organic matter ($\delta^{13}C_{org}$), *n*-alkanes and their carbon isotope ($\delta^{13}C_{ALK}$) in various environments (e.g., Yamamoto et al., 2010; Zhang et al., 2010; Zech et al., 2012).

Jeju Island, the study area of Hanon paleo-maar, is located at the southern part of the Korean Peninsula, and it was situated inside the path of the Asian monsoon winds (westerly jet belt) during the Quaternary. Monsoonal patterns and subsequent results could be preserved in the sediment of this area, providing records of paleo-vegetation and paleoclimate variations. A number of previous studies concerning the Hanon paleo-maar and climate changes on Jeju Island, have identified the climatic variation that are known to be strongly associated with the East Asian monsoon system, and further climatic variation has been driven by low-latitude oceanic force since the late Pleistocene (Lee et a., 2008; Lim and Fujiki, 2011; Park et al., 2014). In particular, several previous studies have focused on vegetation changes and paleoclimatic variations by studying inorganic geochemical proxies and pollen data (e.g., Lee et al., 2008; Lim and Fujiki, 2011; Park et al., 2014). However, these results did not cover the full last glacial maximum (LGM) and are constrained by the limited utilities of proxies. There previous studies didn't provide the paleo vegetation changes by *n*-alkanes approaches. Therefore, to gain a more detailed understanding of the glacial-interglacial variation of paleoclimate and paleovegetation, it is necessary to comparative study using a new proxy to detect past evidence left by the East Asian monsoon.

Assuming that the climate change typical during the glacial-interglacial time periods prevailed on Jeju Island, the vegetation types that are dependent on altitudes might have been different, and this difference might be reflected in the Hanon paleo-maar sediments. Therefore, we used carbon and nitrogen isotope of organic matter and terrestrial *n*-alkane leaf-wax biomarkers and their compound-specific isotope ratios to reconstruct paleo-vegetation changes and the variability of the paleoclimate of the study area in the present study. Further, we will discuss the relationship between this new data with East Asian monsoon variability through a comparison with previous works.

2. Geological setting, sampling, and chronology

The paleo-lake Hanon Maar is located on the southern part of Jeju Island of the Korean Peninsula. This Hanon-Maar is known as one of the largest volcanoes on Jeju Island, where numerous small volcanoes were formed during the Quaternary (Fig. 1A–C). Unlike most other types of volcanoes, active or post-active mountain types, the Hanon volcano is typical maar type, and known to be the only maar type on Jeju Island. Hanon paleo-maar is a volcanic activities-related crater, and its width of rim to rim are about 1.0–1.2 km, and altitudinal contrast between the crater rim and the crater floor is up to about 90 m (Yoon et al., 2006). Based on an electric resistivity survey, the sediment that fills a crater is as thick as about 15 m (Fig. 1D). Therefore, the Hanon paleo-maar was once a water-filled crater, and it can be classified as a tuff ring with a maar crater based on its present morphology (Yoon et al., 2006).

Jeju Island is surrounded by the shallow East China Sea and South Sea of Korea, and its environment is characterized by a warm, humid climate during the summer and by strong winds during the winter due to the Siberian high. Due to these circumstances, the general climatic variations of Jeju Island are strongly associated with Asian monsoon variation as well as oceanic forcing during glacial-interglacial periods (Lee et al., 2008; Lim and Fujiki, 2011). Therefore, climatic change at this site is very sensitive and could reflect East Asian monsoon climatic variation.

The present vegetation of Jeju Island is known to be related to the altitudinal variation of Mt. Halla, which is the only one large mountain on Jeju Island (Kong, 1998). As mentioned, Juju Island was formed by volcanic eruption, and includes one large volcano, Mt. Halla, the height of which is 1950 m above sea level. The types of vegetation on Jeju Island show wide variation in accordance with altitude, with evergreen broadleaf forest at about 700 m above sea level, deciduous forest in a band about 700–1300 m, mixed deciduous and coniferous forest in a band at 1300–1500 m, and bands of coniferous (1500–1800 m) and subalpine scrub and grassland (1800–1950 m) (Oh et al., 2007).

As shown in Fig. 1D, the thickness of sediment layers differs from place to place in the Hanon paleo-maar. Several previous works have shown different core lengths in their studies; Park et al. (2014) used relatively a short core (2.54 m), and Lee et al. (2008) used two cores (about 4.93 m and 6.02 m in depth). Also, Park and Park (2015) used an approximately 10 m-long core for pollen-based temperature reconstruction. Even though their core length were different from core to core, the lithological changes were very similar each other; it contain paleoclimatic information since the last glacial maximum (LGM). However, the ages considered in previous works have differed slightly, and their ages were limited to only in Holocene records; they did not provide paleoenvironmental records for the LGM. To acquire the information about the last glacial and Holocene, we tried to find the deepest possible sediment column and retrieved a 12.5 m-long sediment core in June 2014 based on the results of an electric resistivity survey previously accomplished (Fig. 2).

3. Methods and materials

The 12.5 m long core was collected from the Hanon paleo-maar on July, 2015 year. After the collection, the sediment moved to Jeju National University and cut into two part. Subsamples for the analysis of organic materials were collected directly under the laboratory condition. The subsamples were then dried at 60 °C dry oven for overnight, and crashed for TOC and *n*-alkanes analysis.

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