Influence of aerosol source regions and transport pathway on δD of terrestrial biomarkers in atmospheric aerosols from the East China Sea

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Abstract

We measured stable hydrogen isotope ratios (δD) of terrestrial biomarkers (n-alkanes and n-fatty acids) in atmospheric total suspended particles collected at Jeju Island in the East China Sea, from April 2001 to March 2002, to better understand the influence of long-range atmospheric transport on their seasonal variations. The δD values of the C27, C29 and C31 n-alkanes (δDALK) show a significant negative correlation with the CPI values of n-alkanes (r² = 0.26, p < 0.01), suggesting that the δDALK variations are partly attributed to a superimposed contribution from fossil fuel hydrocarbons. Seasonal variations in the concentrations of the C22–C28 even-carbon numbered n-fatty acids revealed relatively high concentrations in spring, autumn and winter seasons, in which the air masses are transported from northeast Asia. In contrast, the concentrations are low in summer when the air masses are transported from Southeast Asia and the Pacific. Relatively high C26/FA and low C24/FA ratios in spring, autumn and winter samples suggest that the C26 n-fatty acids are more abundantly transported from the Asian continent during these seasons. Seasonal variations in the δD of the C22–C26 even-carbon numbered n-fatty acids exhibit significant enrichment with δD in May and June to August samples, whereas the δD of the C28 n-fatty acids gradually decrease during summer. The magnitude of the δD offsets (~45‰) between the C28 n-fatty acid and the other homologues are much larger than those observed in East Asia spanning 18°N–50°N latitude (ca. 30‰), suggesting that the decoupling is likely attributed to the mixing of distinct source vegetation with different δD ratios. Comparison of the weighted-mean δD values of n-fatty acids (δDFA) between air mass source categories revealed relatively low values (~−170‰) in samples with trajectories from the northeastern part of the Asian continent, supporting that the δD analyses may be a powerful tool in deciphering the source regions of terrestrial biomarkers in atmospheric aerosols from the Asian continent. The results of this study provide important implications for paleoclimate studies that the δD variations of long-range transported terrestrial biomarkers in remote ocean sediments may have recorded past changes in source strengths of the biomarkers and therefore have a potential to reconstruct paleo-wind patterns and transport of terrestrial carbon over the Pacific.

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1. INTRODUCTION

The atmosphere is the most significant pathway for much of the terrestrial carbon transported to the remote oceans (Gagosian and Peltzer, 1986; Duce et al., 1991). An estimated rate of atmospheric delivery of terrestrial carbon to the oceans is ~2.6 to ~10.1×10¹⁴ g·yr⁻¹ (Chester, 2001), about the same order as riverine estimates.

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(4.0 × 10^{14} \text{gy}^{-1}. \text{Hedges et al., 1997}). The airborne particles are eventually scavenged from the atmosphere by precipitation and dry fallout, and deposited into modern and geological samples \cite{Kawamura, 1995}. Hence, understandings of the transport processes of the terrestrial carbon through the atmosphere can provide a base for paleoclimatological studies in ice cores and marine sediments, in addition to information on contemporary processes. However, our knowledge on the source regions and transport pathway of the terrestrial carbon is still limited as compared with those of inorganic minerals.

Homologous series of high molecular weight \textit{n}-alkanes, \textit{n}-alkanols and \textit{n}-fatty acids are major components of terrestrial higher plant epicuticular waxes \cite{Eglinton and Hamilton, 1967}. These organic compounds are easily sloughed off from the surface of plant leaves and transported by long-range winds to remote sites as airborne particles \cite{Simoneit et al., 1977, 2004; Gagosian et al., 1981, 1987; Fang et al., 2002; Schefu et al., 2003). Alternatively, they can be blown up from decaying plant materials in soils by dust storms \cite{Simoneit et al., 1977}, or emitted as smoke particles by forest fires and biomass burning \cite{Abas et al., 1995; Oros and Simoneit, 2001}.

Stable carbon isotope ratios (\delta^{13}C) of terrestrial biomarkers have been particularly used for the last decade to investigate transport processes via wind \cite{Conte and Weber, 2002; Fang et al., 2002; Schefu et al., 2003; Bendle et al., 2006, 2007). This is because the \delta^{13}C of terrestrial biomarkers in the atmosphere can reflect the C_{3}/C_{4} plant compositions of their source vegetation due to large isotopic differences \cite{Simoneit et al., 1977; Gagosian et al., 1981, 1987; Schneider et al., 1983; Kawamura, 1995; Conte and Weber, 2002; Kawamura et al., 2003; Schefu et al., 2003). Alternatively, they can be blown up from decaying plant materials in soils by dust storms \cite{Simoneit et al., 1977}, or emitted as smoke particles by forest fires and biomass burning \cite{Abas et al., 1995; Oros and Simoneit, 2001}.

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In this study, we present seasonal variations of \delta D values of terrestrial biomarkers (\textit{n}-alkanes and \textit{n}-fatty acids) in atmospheric aerosols collected from Jeju Island, and compare the results with molecular compositions and air mass trajectory distributions. The ultimate objective of this study is to explore the influence of changes in aerosol source regions and transport pathway on the \delta D values of terrestrial biomarkers. In addition, this work also provides a base for future paleoclimatological work in ocean sediments and ice cores because these biomarkers are important terrestrial biomarkers to be used in paleoclimatological studies.

2. SAMPLES AND ANALYTICAL METHODS

2.1. Samples

Aerosol sampling was conducted at Gosan site (33°17'N, 126°09'E, Fig. 1b) on a weekly basis from 13 April, 2001 to 21 March, 2002. The site is located at the top of a 72 m cliff on the western edge of the Jeju Island and isolated from residential areas on the island \cite{Kawamura et al., 2004}. Total suspended particles were collected on pre-combusted quartz filters (Pallflex 2500QAT, 20 cm × 25 cm) for 2–9 days using a high-volume air sampler (Kimoto AS-810). The sampler was installed on the roof of a trailer house (~3 m above the ground), and a total of 1235–9212 m\(^3\) of the air was collected from the whole sector at the flow rate of 50 m\(^3\)/h. After the sampling, the filter was placed in a separate clean glass jar with a Teflon-lined screw cap and stored in a freezer room (~20 °C) until analysis.

2.2. Extraction and separation of terrestrial biomarkers

Each sample filter was extracted using DIONEX ASE-200 three times at 100 °C and 1000 psi for 5 min with 0.1 M KOH–methanol solution (10 ml) and by subsequent ultrasonication with dichloromethane (DCM) (10 min). The extracts were combined and concentrated under vacuum and then divided into neutral and acidic fractions \cite{Kawamura, 1995; Kariya, 2007}. The neutral fraction was first separated from the solution by extraction with n-hexane/DCM (10:1) mixture. Aliphatic hydrocarbons (including \textit{n}-alkanes) were isolated using a silica gel (deactivated with 1% H\(_2\)O) column chromatography by elution during winter. This seasonal reversal in prevailing winds is called the East Asian monsoon, having a great impact on compositions and transport pathways of atmospheric aerosols in this region. Jeju Island, South Korea, is a small island located at the northern edge of the East China Sea (Fig. 1b), in which the air masses are generally transported from the Asian continent by westerlies in spring, fall and winter seasons, whereas the air masses are originated from the south during summer due to the influence of the Asian summer monsoon \cite{Black, 2002}. Hence, the atmospheric aerosols from Jeju Island can provide a good opportunity to capture air masses that originate from various source regions, including China, Siberia, Japan as well as Southeast Asian countries.

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In addition to \delta^{13}C, recent studies have suggested that stable hydrogen isotope ratios (\delta D) of terrestrial biomarkers in the atmosphere might also have the potential to provide a key to better understanding source regions \cite{Yamamoto and Kawamura, 2010; Yamamoto et al., 2011}. For example, Yamamoto et al. \cite{Yamamoto et al., 2011} reported large isotopic differences \cite{Conte et al., 2003} in addition to the variations among plant leaves from different plant types \cite{Chikaraishi and Naraoka, 2007} and habitats \cite{Vogts et al., 2009}.

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In the Asian-western North Pacific region, summertime heating of the Asian continent creates a low-pressure system over Siberia that promotes the northward transport of air masses from the Pacific, whereas cold and dry air masses that originate from the Siberian high-pressure system create southerly winds towards the Pacific Ocean
with 1.7 ml of n-hexane. The remaining solution was acidified with 6 M HCl, and the carboxylic acids were extracted with DCM. The acid fraction was then treated with 14% BF₃/methanol to convert carboxylic acids to their methyl esters. Monocarboxylic acid methyl esters were isolated on a silica gel (deactivated with 1% H₂O) column chromatography by elution with n-hexane/DCM (1:2) mixture.

Concentration of n-alkanes and n-fatty acid methyl esters (FAMEs) were quantified by using a gas chromatograph/flame ionization detector (GC/FID, Hewlett–Packard 6890 GC) equipped with an on-column injector and a CP-Sil 5 CB fused silica capillary column (60 m × 0.32 mm i.d., 0.25 μm film thickness). Helium was used as a carrier gas at a flow rate of 1.8 ml/min. The GC oven temperature was programmed from 50 to 120 °C at 30 °C/min, then to 310 °C at 5 °C/min and held isothermally for 45 min. GC data were processed by the Chemstation software, and the carbon preference index (CPI) was calculated as follows:

\[
\text{CPI}_{\text{ALK}} = 0.5 \times \frac{\sum (C_{25} - C_{35})_{\text{odd}}}{\sum (C_{24} - C_{34})_{\text{even}}} + \frac{\sum (C_{25} - C_{35})_{\text{even}}}{\sum (C_{26} - C_{36})_{\text{even}}}
\]

where C is abundance of each n-alkane (Bray and Evans, 1961);

\[
\text{CPI}_{\text{FA}} = 2 \times \frac{\sum (C_{20} - C_{30})_{\text{even}}}{\sum (C_{19} - C_{29})_{\text{odd}} + \sum (C_{21} - C_{31})_{\text{odd}}}
\]

where C is concentration of each n-fatty acids. Structural identification of n-alkanes and n-fatty acids was performed with a GC/mass spectrometer (GC/MSD, Hewlett–Packard 6890 GC/5973 Mass Selective Detector) equipped with a HP-5MS fused silica column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The temperature program was the same as for GC analysis. The components were identified by the comparison of their GC retention times and mass spectra with those of reference compounds.
2.3. Compound-specific stable hydrogen isotope analysis

Stable hydrogen isotope (δD) analysis of n-alkanes and n-fatty acid methyl esters (FAMEs) was performed on thirty samples that contain sufficient amount of target compounds (>35 ngH; Yamamoto and Kawamura, 2012). Only the n-alkane fractions were purified by using the method described in Yamamoto and Kawamura (2012) to remove unresolved complex mixture (UCM) of hydrocarbons that interfere the accurate isotope measurements of n-alkanes. Briefly, a saturated solution of urea in methanol was added to the hydrocarbon fraction dissolved in n-hexane/acetone (2:1) and gently stirred overnight to complete the adduction. After adduction, the solvent was removed from the urea precipitate, which was rinsed with fresh solvent to remove non-adducted materials. The urea crystals were dried under a N2 stream and the n-alkanes were recovered in n-hexane after dissolution of the crystals in water.

The D/H ratios of n-alkanes and FAMEs were determined with a GC/thermal conversion/isotope ratio mass spectrometer system (Hewlett-Packard 6890 GC/Finnigan MAT Delta Plus XL IRMS) equipped with DB-5MS fused silica capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness) and DB-5HT fused silica capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness), respectively. For the determination of the δD of n-alkanes, the GC oven temperature was programmed from 50 to 120 °C at 10 °C/min, and to 310 °C (held 45 min) at 4 °C/min. Helium was used as a carrier gas at a flow rate of 1.5 ml/min. In contrast, for the determination of the δD of FAMEs, the GC oven temperature was programmed from 50 to 120 °C at 30 °C/min, and to 310 °C (held 20 min) at 5 °C/min, with carrier gas (helium) flow rate of 1.2 ml/min. One to two microliters of samples were injected with an internal standard (C20 n-fatty acid methyl ester; δD = −166.7‰ for n-alkanes and C32 n-alkanes; δD = −220‰ for FAMEs). The eluting compounds were transferred to a high-temperature conversion furnace and quantitatively converted to H2 in a microvolume ceramic tube held at 1450 °C. A standard consisting of C16–C34 n-alkanes was daily injected into the GC/IRMS to check the data quality and to evaluate instrument performance. Analytical accuracy and precision of the standards was ±5‰ and 4‰, respectively. The δD values are expressed as per mil (‰) relative to the Standard Mean Ocean Water (SMOW). The measured δD values of FAMEs were corrected for the contribution of hydrogen (δD = −225‰) added during methyl esterification using the mass balance equation (Yamamoto et al., 2011). Most measurements were duplicated, and the mean values are reported.

2.4. Air mass trajectory analysis

Ten-day back air mass trajectories were calculated in order to determine transport pathways of air masses that arrived to Gosan site during sampling periods. The backtrajectory analyses were conducted daily using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Rolph, 2003; Rolph, 2003). Initial position of air masses was allocated at 500 m height above the sampling site, and the trajectories were calculated using the model vertical velocity and the NOAA reanalysis data.

3. RESULTS

3.1. Molecular distribution of n-alkanes and their stable hydrogen isotope ratios

Aliphatic hydrocarbon fractions in marine aerosols from Jeju Island are mainly composed of terrestrial higher plant n-alkanes (C25–C35 n-alkanes with high CPI values; Eglin and Hamilton, 1967) with minor contribution from fossil fuel hydrocarbons (e.g., C10–C35 n-alkanes with low CPI values; Simoneit and Mazurek, 1982; Kawamura and Kaplan, 1991). The CPI values for the C25–C33 n-alkanes (CPIalk,C) range from 1.8 to 4.1, and show relatively high values in early spring, summer and autumn samples (Table 1). The C29 or C31 n-alkanes are generally found as the most abundant homologue, however, the C27 n-alkane dominates over these n-alkanes in the sample collected in 25–26 April, 2001 (KOS018).

Stable hydrogen isotopic compositions (δD) of the C23–C35 n-alkanes range from −45‰ to −207‰. The δD values of the C23–C35 odd-carbon numbered n-alkanes are generally depleted in deuterium by up to 74‰ as compared with those of even-carbon number homologues. The degree of depletion gradually increased from the C23 n-alkane to the C27 n-alkane and maximized at C29 or C31 (Fig. 2a).

3.2. Molecular distribution of n-fatty acids and their stable hydrogen isotope ratios

Monocarboxylic acid fractions in marine aerosols from Jeju Island are mainly composed of homologous series of C12–C34 n-fatty acids. Molecular distributions of n-fatty acids exhibit a strong even/odd carbon number predominance (CPIFA > 2.6; Table 1; Fig. 2b) with two or three maxima, generally at C16 and C24, and at C16, C24 and C30, respectively. Lower molecular weight n-fatty acids are generally typical in various organisms including marine phytoplankton and bacteria as well as terrestrial higher plants. However, their high molecular weight homologues (>C24) are thought to originate from terrestrial higher plant waxes (Eglin and Hamilton, 1967; Simoneit and Mazurek, 1982).

Stable hydrogen isotopic compositions (δD) of n-fatty acids were only measured for the C22–C28 even-carbon number species because low concentrations and co-elution with unsaturated compounds did not allow obtaining meaningful isotope values for the other compounds. The δD values of the C22–C28 even-carbon numbered n-fatty acids range from −134 to −189‰, and show gradual decrease with an increase in the number of carbon atoms (Fig. 2b).

3.3. Air mass back trajectories

Air mass trajectories were sorted into three categories in terms of wind direction and the regions where they passed...
<table>
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<th>Sample</th>
<th>Start date</th>
<th>n-Alkanes (ng m⁻³)</th>
<th>CPI_{ALK}²</th>
<th>δD (‰)</th>
<th>n-Alkanic acids (ng m⁻³)</th>
<th>CPI_{PA}³</th>
<th>δD (‰)</th>
<th>Air mass trajectory (%) of total trajectories</th>
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<td>159</td>
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<td>ND</td>
<td>-139</td>
<td>115</td>
<td>9.8</td>
<td>3.6</td>
<td>151 (0)</td>
</tr>
<tr>
<td>KOS108</td>
<td>15 March, 2002</td>
<td>2.9 14.5 0.0 2.6</td>
<td>ND</td>
<td>-189</td>
<td>176</td>
<td>28.8</td>
<td>3.6</td>
<td>172 (0)</td>
</tr>
<tr>
<td>KOS111</td>
<td>21 March, 2002</td>
<td>2.1 15.9 0.0 6.2</td>
<td>ND</td>
<td>-163</td>
<td>175</td>
<td>63.2</td>
<td>4.2</td>
<td>175 (0)</td>
</tr>
</tbody>
</table>

Note: ND, not determined.

1. CPI_{ALK} = 0.5 × \sum(C_{25} - C_{33}) + \sum(C_{24} - C_{26}) + \sum(C_{19} - C_{29}) + \sum(C_{17} - C_{23}) + \sum(C_{19} - C_{23})

2. CPI_{PA} = 2 × \sum(C_{25} - C_{26}) + \sum(C_{24} - C_{25}) + \sum(C_{23} - C_{27}) + \sum(C_{27} - C_{33})

3. A, western trajectory from China and Far East Russia; B, trajectory over the vicinity of the East China Sea and Sea of Japan; C, trajectory from Southeast Asia and the Pacific.

4. Numbers in parentheses indicate % of the trajectories over land at >500 m altitude in each categories.
are systematically depleted in deuterium by \( \sim 25\% \) relative to the corresponding carbon-numbered \( n \)-alkanoic acids (Chikaraishi and Naraoka, 2007). Thus, both the values should be positively correlated if they primarily reflect the \( \delta D \) values in their source vegetation. The \( \delta D_{\text{ALK}} \) and the \( \delta D_{\text{FA}} \) values in our samples show a very strong positive relation \( (r^2 = 0.5, p < 0.01; \text{Fig. 5a}) \), although the relation is not so strong as compared with those observed in contemporary plant leaf waxes \( (r^2 > 0.7; \text{Chikaraishi and Naraoka, 2007}) \). Because high molecular weight \( n \)-fatty acids are not produced by any of anthropogenic activities \( \text{e.g., the use of fossil fuels and cooking operations; Rogge et al., 1991, 1993} \), the differences between the aerosols and plant leaves may be attributed to contribution of anthropogenic hydrocarbons.

In order to evaluate potential influence of anthropogenic hydrocarbons on the \( \delta D \) of \( n \)-alkane biomarkers, we investigated their relation with the CPI values of \( n \)-alkanes \( (\text{CPI}_{\text{ALK}}) \). This is based on rationale that the CPI values are generally high \( (\text{CPI} > 5; \text{Eglington and Hamilton, 1963; Mazurek and Simonet, 1984}) \) when there is no serious input from fossil fuel hydrocarbons \( (\text{CPI} = 1; \text{Simoneit and Mazurek, 1982; Kawamura and Kaplan, 1991}) \). The weighted-mean \( \delta D \) values of the \( C_{27}, C_{29} \) and \( C_{31} n \)-alkanes \( (\delta D_{\text{ALK}}) \) show a significant negative correlation with the \( \text{CPI}_{\text{ALK}} \) values \( (r^2 = 0.26, p < 0.01; \text{Fig. 5b}) \), suggesting a superimposed contribution from anthropogenic sources, in addition to original plant signals.

In previous study, Yamamoto and Kawamura (2010) corrected the contribution from anthropogenic hydrocarbons on the \( \delta D_{\text{ALK}} \) in urban aerosols from Tokyo using a mass-balance approach with the assumption that the \( \delta D \) values of even-carbon numbered \( n \)-alkanes mainly reflect the \( \delta D \) of fossil fuel \( n \)-alkanes. However, this method may not be applicable to our samples because the relation between the \( \delta D_{\text{ALK}} \) and the \( \text{CPI}_{\text{ALK}} \) values in the aerosols from Jeju Island is not so tight as observed in Tokyo \( (r^2 = -0.76) \). In addition, the \( \delta D \) values of even-carbon
numbered n-alkanes in our samples show large seasonal variations by up to 60%, suggesting that the n-alkanes are likely derived from different fossil fuel sources and/or combustion processes. Hence, we only use the δDFA values in the following discussion.

4.2. Variations in concentrations and molecular compositions of n-fatty acids in aerosols from Jeju Island

Fig. 6b shows temporal variations in the concentrations of the C_{22−28} even-carbon numbered n-fatty acids in aerosols collected at Jeju Island from April 2001 to March 2002. The concentrations ranged from 8.3 to 131.5 ng m^{-3} (Table 1; Fig. 6b), which are significantly higher than those observed in Chichi-Jima (27°04’N, 142°13’E; ~24.3 ng m^{-3} for C_{20−32} n-fatty acids; Kawamura et al., 2003) and Marshall Islands (11°20’N, 162°20’E; ~0.67 ng m^{-3} for C_{21−32} n-fatty acids; Gagosian et al., 1981) in the Pacific. In general, abundant terrestrial biomarkers are long-range transported from the Asian continent to the western North Pacific by westerlies (Kawamura et al., 2003). Hence, the higher concentrations suggest that the atmospheric aerosols from Jeju Island are strongly influenced by long-range atmospheric transport from the Asian continent as compared with the other two remote ocean sites.

The C_{22−C_{28}} even-carbon numbered n-fatty acids revealed relatively high concentrations in spring, autumn and winter seasons, whereas the concentrations are low in summer (Fig. 6b). The high concentrations are generally observed when the air masses are transported from northeast Asia (Fig. 6a and b), which suggests that the terrestrial biomarkers are abundantly transported during spring, autumn and winter seasons by westerlies. In contrast, the concentrations do not show any clear relation with the height of trajectories (Table 1), which underscores high variability in biomarker concentration among individual air masses.

Fig. 6b shows temporal variations of the concentration ratios of the C_{24} and C_{26} n-fatty acids to the total C_{22−C_{28}} even-carbon numbered n-fatty acids (C_{24}/FA and C_{26}/FA). We found relatively high C_{24}/FA and low C_{26}/FA ratios in association with category C trajectories, whereas relatively low C_{24}/FA and high C_{26}/FA ratios are
observed in spring, fall and winter seasons (Fig. 6a and b). The good correspondence between the $C_{24}/FA$ and $C_{26}/FA$ ratios and the seasonal changes in air mass transport implies that source regions of the $n$-fatty acids may be shifted

Fig. 4. Variations in (a) the distribution of air mass trajectory sectors, (b) the concentrations of $C_{21}$–$C_{24}$ $n$-alkanes and UCM, and the carbon preference index (CPI) values, and (c) the $\delta D$ values of $C_{27}$, $C_{29}$ and $C_{31}$ $n$-alkanes in aerosol samples collected in Jeju Island from April 2001 to March 2002.

Fig. 5. Cross-plots of (a) the weighted-mean $\delta D$ ratios of $C_{27}$, $C_{29}$ and $C_{31}$ $n$-alkanes versus the weighted-mean $\delta D$ ratios of $C_{22}$–$C_{28}$ even-carbon numbered $n$-fatty acids, and (b) the weighted-mean $\delta D$ ratios of $C_{27}$, $C_{29}$ and $C_{31}$ $n$-alkanes versus CPI values of $n$-alkanes.
seasonally due to the changes in the air mass transport pathways. In support for this, previous studies reported that the molecular distribution of \( n \)-fatty acids in the atmospheric aerosols significantly varies between aerosol source regions in the western North Atlantic (Conte and Weber, 2002). Hence, our results suggest that the \( C_{24}/FA \) and \( C_{26}/FA \) ratios in aerosols may be used to distinguish aerosol source regions in the coastal regions of the western North Pacific rim.

4.3. Variations in stable hydrogen isotope ratio (\( \delta D \)) of \( n \)-fatty acids in aerosols from Jeju Island

Fig. 6c shows temporal variations in the \( \delta D \) values of \( C_{22}-C_{28} \) even-carbon numbered \( n \)-fatty acids in aerosol samples collected at Jeju Island from April 2001 to March 2002. The \( \delta D \) values of \( n \)-fatty acids in aerosols from Jeju Island show large variations in different carbon-numbered homologues within samples (i.e., the \( C_{22} \) or \( C_{26} \) \( n \)-fatty acids are the most D-enriched compounds in spring, autumn and winter samples, while the \( C_{24} \) \( n \)-fatty acid is the most D-enriched compound in summer samples; Fig. 6c). The \( \delta D \) variations exhibit a good agreement with the air mass trajectories (Fig. 6a and c), suggesting that the variations are likely related to seasonal shifts in the source regions of the \( n \)-fatty acids.

The \( \delta D \) values of leaf wax \( n \)-alkanes are generally determined only early in the ontogeny of a leaf (Kahmen et al., 2011) and the values are ‘locked in’ within a leaf generation (Sachse et al., 2010). However, environmental stress or physical damage of the cuticle can stimulate the production of leaf waxes even in mature leaves (Cameron et al., 2006; Shepherd and Griffiths, 2006). Similar \( \delta D \) variations in the different homologues are also reported in contemporary
plant species and in different seasons within a single plant species (Chikaraishi and Naraoka, 2007), suggesting that the δD variations might be explained by differences in timing of production (Bianchi et al., 1989; Gitzl et al., 1991; Masle and Scannellier, 1992), the de novo synthesis of leaf waxes against exposure to environmental stress (such as temperature and water stress) and the physical abrasion of cuticular waxes, and seasonal changes of organic substrate (Sessions, 2006). Rapid turnover of n-alkyl compounds on time scale of several weeks (Lockheart et al., 1997; Sachse et al., 2009) could also be a possible explanation for the variations.

Seasonal δD profiles of the n-fatty acids in aerosols from Jeju Island revealed decoupled fluctuation pattern between the C28 n-fatty acid and the C22, C24 and C26 n-fatty acids (Fig. 6c). The δD offsets between the C28 n-fatty acid and C24 and C26 n-fatty acids show significant increases (~45‰) in summer samples in which the air masses are transported northward from Southeast Asia and the Pacific (Fig. 6c). In East Asia, the δD values of terrestrial higher plant waxes generally decrease from low to high latitude by reflecting the δD of precipitation (West et al., 2008; Rao et al., 2009). Hence, one possible explanation for the decoupling would be the transport of relatively D-enriched C22–C26 even-carbon numbered n-fatty acids from the low latitudes in summer. However, the magnitude of the δD offsets between the C28 n-fatty acid and other homologues are much larger than those observed in East Asia spanning 18°N–50°N latitude (ca. 30‰). Recent studies on the δD of contemporary higher plant waxes have reported that apparent isotopic fractionations (the δD differences between lipids and source water) differ significantly among different plant species, even though they have grown at the same location (Hou et al., 2007; Pedentchouk et al., 2008; Feakins and Sessions, 2010). Thus, the decoupling is more likely attributed to the mixing of distinct source vegetation having different molecular and δD compositions, rather than the differences in the δD of their source water.

4.4. Influence of transport pathways on the δD of the n-fatty acids in aerosols from Jeju Island and implications for palaeoclimatic studies

Seasonal variations in the weighted-mean δD values of the C22–C28 even-carbon numbered n-alkanoic acids (δDFA) in aerosols collected at Jeju Island from April 2001 to March 2002 show significant increases (−132‰) in May and June to August samples (Fig. 6c). Because the δD values of terrestrial higher plants mainly reflect the δD ratios of precipitation with modification by D-enrichment of the source water through transpiration and soil evaporation (Sachse et al., 2006), and biosynthetic isotopic fractionation during photosynthesis and lipid biosynthesis (Chikaraishi and Naraoka, 2003), the observed changes in the δDFA values is likely caused by changes in these environmental and biological factors.

In East Asia, the δD values of terrestrial higher plant waxes generally decrease from low to high latitude by reflecting the δD of precipitation (West et al., 2008; Rao et al., 2009). Because the source regions of the n-fatty acids shifted from north to south during summer in association with changes in air mass trajectories (see Section 4.2), the δD values of source water should be D-enriched when the source regions were in the lower latitudes. In addition, seasonal changes in the δD of precipitation (IAEA, 2008) and differences in biosynthetic isotopic fractionation within plant types and plant life forms, and seasons (Sessions, 2006; Smith and Freeman, 2006; Hou et al., 2007; Liu and Yang, 2008; Pedentchouk et al., 2008; Sachse et al., 2009) could also be the factors affecting the δDFA variations.

In order to evaluate the influence of transport pathways on the δDFA values, we present box plots of the weighted-mean δD values of C22–C28 even-carbon numbered n-fatty acids for different air mass source categories in Fig. 7. Although there are only a few instances for categories B and C samples after we excluded the samples that received air mass input from multiple source regions, the δDFA values in the samples with trajectories from Northeast Asia (category A; Fig. 3) are found to be significantly lower (by ~40‰) than those in the samples with trajectories from the vicinity of Korea and Japan, and from Southeast Asia and the Pacific (categories B and C; Fig. 3).

It is notable that the δDFA values exhibit clear differences between different categories of air mass trajectories despite that the δD of plant waxes may be controlled by various environmental and biological factors (e.g., relative humidity, plant physiology and plant life forms). Because air masses moving across the land surface can generally accumulate and integrate higher plant signals from vegetation
and soils over wide geographic regions (Scheffü et al., 2003; Matsumoto et al., 2001), such factors may be averaged, resulting in less variability in the δDFA values in the atmospheric aerosols. In support for this, Yamamoto and Kawamura (2010) reported only small seasonal changes in the δD of airborne leaf wax n-alkanes from Tokyo where the n-alkanes are primarily originated from local vegetation.

Previous study on the δ13C of terrestrial biomarkers in Chichi-Jima in the western North Pacific, reported difficulty in distinguishing northeast and southeast sources of the Asian continent based on the δ13C because there is a major overlap in the interquartile ranges of these two categories (Bendle et al., 2006). However, our results showed that the δDFA values exhibit a large difference between samples with northeast and southeast trajectories (Fig. 7), supporting that the δD analyses might be a powerful tool in deciphering the source regions of terrestrial biomarkers in atmospheric aerosols from the Asian continent.

On the other hand, the δD values of terrestrial biomarkers in marine and lacustrine sediment have also been used to reconstruct δD of precipitation in the past (e.g., Sachse et al., 2006) because terrestrial higher plant primarily reflect the δD of precipitation waters on their D/H ratios with minor modification by local and regional meteorology (evaporation, relative humidity and soil moisture; Sachse et al., 2006). However, the results of this study suggest that caution should be paid in interpreting the δD records in remote ocean sediments because the δD variations of terrestrial biomarkers may have been significantly affected by temporal changes in source strengths of biomarkers, rather than the temporal variations in the δD of source waters.

Terrestrial biomarkers that are transported to the remote oceans via wind are eventually sequestered in marine sediments. Hence, the δD of n-fatty acids in the Pacific sediments, which are largely supplied by atmospheric transport followed by dry/wet deposition and the subsequent settling in the water column (Kawamura, 1995), may have a potential to reconstruct paleo-wind patterns and transport of the terrestrial carbon from the Asian continent.

5. SUMMARY AND CONCLUSIONS

In this study, we examined seasonal variations in the δD values of terrestrial biomarkers (n-alkanes and n-fatty acids) in atmospheric aerosols from Jeju Island in the western North Pacific rim in terms of changes in aerosol source regions and transport pathway.

Although we observed a very strong positive relation between the δD values of the C27, C28 and C31 n-alkanes (δDALK) and the C22-C28 even-carbon numbered n-fatty acids (r² = 0.5, p < 0.05), a significant negative correlation was found between the δDALK and the CPI values (r² = 0.25, p < 0.01). The relation suggests that the δDALK values likely reflect a superimposed contribution from fossil fuel sources, in addition to original plant signals, which highlights the advantages of δD of n-fatty acids over n-alkanes to study the source vegetation in the atmospheric aerosols.

Seasonal variations in the concentrations of the C22–C28 even-carbon numbered n-fatty acids show relatively high concentrations in spring, autumn and winter, suggesting that the terrestrial biomarkers are abundantly transported during these seasons by westerlies. Specifically, relatively low C26/FA and high C20/FA ratios in spring, fall and winter suggest that the C26 n-fatty acids are more abundantly transported from the Asian continent.

Seasonal δD profiles of the n-fatty acids in aerosols from Jeju Island revealed decoupled fluctuation pattern between the C28 n-fatty acid and the C22, C24 and C26 n-fatty acids. The magnitude of the δD offsets (~45‰) between the C28 n-fatty acid and the other homologues in summer samples are much larger than those observed in East Asia in latitudinal range of 18°N–50°N (ca. 30‰), suggesting that the decoupling is likely attributed to the mixing of distinct source vegetation with different δD ratios.

Comparison of the weighted-mean δD values of the C22–C28 even-carbon numbered n-alkanoic acids (δDFA) between air mass categories revealed a large gap (~40‰) between the samples with the air mass trajectories from the northeastern part of the Asian continent (category A) and those with trajectories from other source regions (categories B and C). This result suggests that atmospheric transport pathway is one of the important factors that determine the δDFA in aerosols from Jeju Island, supporting that the δD analyses may be a powerful tool to distinguish northeast and southeast source of terrestrial biomarkers in atmospheric aerosols from the Asian continent.

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