Eolian transport of higher plant terpenoids (HPTs) in the northwestern Pacific off central Japan

K. SAWADA

Division of Earth and Planetary Sciences, Graduate School of Science, Hokkaido University
(sawadak@ep.sci.hokudai.ac.jp)

Introduction

Atmospheric transport of particles from land to ocean has been often evaluated from the biomarkers of terrestrial higher plant waxes as long-chain alkanes, fatty alcohols and acids. However, there were a few studies on (paleo)climatological and atmosphere chemical investigations from higher plant terpenoids (HPTs), which were peculiar biomarkers of higher plants with structural variety. In this study, HPTs were analyzed in deep sea sediments off central Japan to reconstruct the historical variations of the transport fluxes of terrestrial materials, and to examine their applicability as proxies for assessing the eolian transport of terrestrial particles to ocean.

Materials and Methods

Surface sediments collected from Nishishichitou Ridge across a latitudinal transect at 138°35’E (LM-5P: 32°40’N, LM-4: 30°23’N, and LM-3: 29°45’N) were analyzed. Also, sediment cores collected from the same sites (KT92-17 St. 14: 32°40’N and St. 20: 30°23’N) were used.

Lipids were extracted with dichloromethane / methanol, and separated to acidic and neutral fractions. The neutral fractions were further fractionated to aliphatic and aromatic hydrocarbons, ketones and polar lipids as alcohols. HPTs were identified by GC/MS and quantified by GC.

Results and Discussion

Angiospermous HPTs as oleanenes, oleandienes and ursenes were mainly identified in all surface sediments. Gymnospermous HPTs could not be detected. In general, the oleanenes and ursenes were diagenetically formed from biological terpenoidal alcohols as amyrins, which were commonly appeared in coastal sediments. However, no terpenoidal alcohols could be detected, and oleanoidal ketones were contained in only LM-5P. These results implied that the HPTs that had been experienced significant diagenesis and attached to soils were mainly transported from land to deep ocean through eolian systems.

HPT fluxes in St. 14 and St. 20 tended to increase during the glacial periods, which were almost similar to the variation patterns of fluxes for long-chain alkanes, and fatty alcohols and acids. Also, oleandiene / oleanene ratios, which possibly varied depending on maturity levels and could be ‘freshness’ indicators, were higher in glacial periods. Thus, the ‘fresh’ HPTs might be efficiently supplied to the northwestern Pacific with eolian transport during the glacial periods.

From these findings, it was suggested that the HPT hydrocarbons could be strong proxies of eolian transport.

Measurement and significance of $^{13}C^{18}O^{16}O$ in thermodynamically equilibrated and environmental CO_2

EDWIN A. SCHAUBLE, JOHN M. EILER AND NAMI KITCHEN

Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California USA
(edwin@gps.caltech.edu)

Precise measurements of the abundances of mass 44, 45, 46, and 47 CO_2 molecules have led to the discovery of non-random mixing of the stable isotopes of carbon and oxygen in CO_2 extracted from ambient air as well as CO_2 equilibrated with H_2O in the laboratory. Mass-47 excesses (dominantly $^{13}C^{16}O^{18}O$) of ca. 1‰ are evident in samples that have experienced isotope exchange at low temperatures (i.e., human breath, CO_2 residual of photosynthesis, CO_2 equilibrated with liquid H_2O), relative to samples exchanged at higher temperatures (hydrocarbon combustion products, CO_2 heated to 1000ºC). These results agree with theoretical calculations of equilibrium isotopic mixing, suggesting that mass-47 CO_2 may gauge the relative importance of high-temperature and low-temperature sources to atmospheric CO_2. CO_2 from ambient air is intermediate between the high-T and low-T extremes.

Calculated partition functions for the reaction:

$$^{13}C^{16}O^{16}O + {}^{12}C^{16}O^{18}O \leftrightarrow {}^{13}C^{16}O^{18}O + {}^{12}C^{16}O^{16}O$$

predict an equilibrium constant of about 1.001 at room temperature, decreasing to unity at high temperatures. This results in an excess of mass-47 CO_2 with respect to isotopically randomized CO_2 with the same bulk oxygen and carbon isotope ratios. Non-equilibrium processes will also cause deviations from random isotopic mixing. Diffusion through a small orifice results in a 0.4‰ mass-47 excess in the diffused gas, leaving a 47-depleted residue. Unequilibrated mixtures of high $\delta^{13}C$, high $\delta^{18}O$ CO_2 with low $\delta^{13}C$, low $\delta^{18}O$ CO_2 are mass-47 enriched, and can be used to monitor internal isotope exchange processes. Similar effects are expected in O_2, N_2, CO, N_2O, O_3, and other strongly-bonded molecules containing two or more atoms of low atomic number with multiple stable isotopes.

Measurements are made using gas source mass spectrometry; six collectors simultaneously measure all of the stable isotopic forms of CO_2 (masses 44 - 49). Precisions for masses 47 and 48 are typically 0.1‰ and 0.4‰, respectively; mass 49 is used to monitor isobaric interferences. Among CO_2 species with masses > 46, mass 47 measurements are the most robust, and show nearly linear instrumental response over the range of terrestrial compositions. Mass 47-labelled samples show that CO_2 is not isotopically scrambled during preparation and measurement. Isotopically randomized standards are prepared by heating CO_2 to 1000ºC. CO_2-H_2O equilibrations at 25ºC and 35ºC suggest that internal equilibration is essentially complete within one day, similar to oxygen-isotope exchange.