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Variations in higher plant terpenoid compositions in the eastern equatorial Pacific sediments over the last 30 Ma

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We analyze terrestrial plant-derived biomarkers (higher plant terpenoids; HPTs) in sediments recovered during the IODP Expeditions 320/321, the Pacific Equatorial Age Transect (PEAT), to reconstruct variations in terrestrial input in the eastern equatorial Pacific Ocean, as well as to evaluate transport systems of terrigenous matter from land to ocean. Terrestrial plant-derived organic molecules in these pelagic areas are considered to be mainly transported through atmosphere by aeolian system. The HPTs such as sesqui-, di- and triterpenoid are major constituents of plant resin, cuticle and supportive tissues. These groups possess different taxonomic origin (i.e. gymnosperms and angiosperms), so that their compositions in the PEAT sediments could be recorded climatic system such as wind strength and direction, and atmospheric circulation, and moreover, the environmental information in the hinterland of continental area(s).

In this study, we perform organic solvent extraction from freeze-dried sediment samples, and separate the extract to four fractions by using silica gel column chromatography. Each separated fractions are analyzed by gas chromatography / mass spectrometer (GC/MS). Because of extremely low concentration and frequent coelution for the HPTs, we quantify by selected ion monitoring (SIM) chromatogram with the representative ions of the compounds.

We could identify the HPTs such as cadalene (sesquiterpenoid), abietane type diterpenoids and oleanane type triterpenoids. The total concentrations of HPTs were 0.03-7.90 ng/g and increased over the last 10 Ma. Paleo-latitudinal distributions of the ratios of the Ole/(DT+Ole) ratio, which is oleanoids to the sum of the oleanoids and diterpenoids, show the highest values near the equator (1^{o}S to 3^{o}N). Oleanoids are relatively abundant only in 0^{o}N to 2^{o}S until the middle Miocene, while the northernmost latitudinal samples are predominated by gymnosperm-derived diterpenoids. Oleanoid-dominant samples appear in northern latitude (0^{o}N to 3^{o}N) during the late Miocene and Pleistocene sediment samples. The result agreed with the general trends of higher plant wax-derived n-alkane ratios ($C_{31}/(C_{29} + C_{31})$), in which the lowest values were observed near the equator, presumably associated with zonal transport of higher plant wax from the tropical South America. The oleanoids mainly originate from angiosperm wax, and therefore, the transport mechanism may be the same as n-alkanes. The rainforest is major vegetation in The tropical South America is characterized by the major cover of rainforest which vegetation is predominated by the angiosperms. Atmospheric transport via aeolian dust from the semiarid and arid region of the central East Asia and North America can also contribute in significant portion of n-alkanes and HPTs in the eastern equatorial Pacific Ocean. The HPTs transported from such arid and/or cool hinterlands might be more abundant in diterpenoids, compared to that from tropical South America. In the study area, the intertropical convergence zone (ITCZ) behaves as a barrier to southward transport of dust from the Asia with its high rainfall, resulting higher deposition of aeolian dust in the latitude. The a little northward areas from the suggested zonal transport shows higher concentrations of HPTs and low Ole/(DT+Ole) ratio. Hence the latitudinal positions of the paleo-ITCZ may correspond to this area.

It is suggested that the latitudal shift of locations that HPT concentrations and compositions are associated with the change in atmospheric circulation in study area, and that the ITCZ located southward during the early to middle Miocene.

Keywords: Pacific Equatorial Age Transect (PEAT), InIntertropical Convergence Zone, aeolian transport, Higher Plant Terpenoid