

A different behavior in isotope exchange of hydrogen between fluoranthene and pyrene

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Polycyclic aromatic hydrocarbons (PAHs) are one of the most ubiquitous organic compounds in the universe. They occur in the extraterrestrial materials as well as terrestrial environments such as sediments and automobile exhausts. Compound-specific carbon isotopic analyses of PAHs have been reported from various samples since last 10 years. The carbon isotopic compositions of individual PAHs are a useful means to investigate their sources as well as formation mechanisms. In particular, two series of PAH formation ("pyrene series" and "fluoranthene series") are distinguished (Naraoka, in this volume) using the carbon isotopic composition. In contrast, compound-specific hydrogen analysis of PAHs has not been reported. As preliminary δD data of PAHs in carbonaceous chondrites also show the two series of PAH, we conducted isotope exchange experiments of hydrogen in PAHs in this study. Two PAH isomers (pyrene and fluoranthene; $C_{16}H_{10}$) were heated with various isotopically modified water in neutral or acidic conditions. Compound-specific hydrogen analysis was carried out by gas chromatography-pyrolysis-isotope ratio mass spectrometry.

Results and discussion

Hydrogen isotope exchange could hardly occur at 170°C under both neutral (pH=7) and weak acidic (pH=4) conditions. Under acidic (pH=2) condition at 170°C and 220°C, however, hydrogen exchange occurred, where pyrene was enriched in D relative to fluoranthene with D-enriched water ($\delta D = +88\%$, $+425\%$ and $+2068\%$). This result suggests that protons in the acidic solution play an important role for exchange reaction, being attributable to electrophilic substitutions on PAHs. In contrast, with D-depleted water ($\delta D = -378\%$) at 220°C, hydrogen exchange also occurred, where pyrene was depleted in D relative to fluoranthene. These results indicate that hydrogen of pyrene exchange with water much faster than that of fluoranthene. δD values of resultant PAHs show apparently constant after 48h. After heating, however, the pH of solutions became neutral (pH \approx 7), so δD value of PAH did not appear to change. Nevertheless, this kinetically-controlled different behavior of hydrogen isotope exchange between pyrene and fluoranthene also suggests two-series PAH formation mechanisms in natural environments.

Determination of platinum in the marine environment with two different methods

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The marine chemistry of the platinum group elements (PGEs) is the least understood of the trace metals because of their very low concentrations. Since the recent progress in the analytical methods and clean technique have made it possible to determine these novel metals in seawater, marine PGE researches are able to focus on some topics, such as tracers of extraterrestrial material and anthropogenic release to marine environments (Ravizza, 2001). However, the vertical profiles of PGEs in the ocean were not clearly understood yet. For example, vertical profiles of platinum by three different groups show variability among the various ocean basins. These contrasting vertical profiles are possibly due to the different analytical methods employed by each group rather than true variability.

In this study, we determined platinum in the estuary, particularly in the areas where the Tama and Ara rivers are flow into Tokyo Bay, with two different analytical methods. The isotope dilution inductively plasma mass spectrometry (ID-ICPMS; Colodner et al., 1993) and the cathodic stripping voltammetry (CSV; van den Berg and Jacinto, 1988) were modified and applied to the estuarine samples. The results by both methods are generally consistent, but the concentrations by the ID-ICPMS were higher than those by CSV, which may reflect the difference in the labile fraction of platinum or the interference of organic substance.

References

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