

HYDROGEN ISOTOPE EXCHANGE OF POLYCYCLIC AROMATIC HYDROCARBONS UNDER HYDROTHERMAL CONDITIONS : IMPLICATIONS FOR CARBONACEOUS CHONDRITES

M. Lecasble, L. Remusat and S. Bernard. Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Sorbonne Universités, CNRS UMR 7590, Muséum National d'Histoire Naturelle, Paris.
E-mail : marceau.lecasble@mnhn.fr.

Introduction: Polycyclic aromatic hydrocarbons (PAHs) are fused benzene rings molecules widely distributed in the interstellar medium (ISM) [1]. They may have been produced through the photolysis of simple gas-phase molecules and interstellar dust mantles or in circumstellar outflows of AGB stars [2]. In the ISM, PAH deuterium enrichment likely occurs due to low-temperature astrochemical processes such as gas phase ion-molecule and gas-grain reactions [3, 4]. PAHs are commonly detected in carbonaceous chondrites (CC) [5, 6] where they take part in the soluble organic matter (SOM). Recently, the hydrogen isotope ratio of pyrene and fluoranthene, the two most abundant PAHs in CCs, has been measured in the CMs Kolang, Mukundpura and Aguas Zarcas and is found depleted in deuterium, reaching δD_{VSMOW} values between -150‰ and -300‰. The loss of their hydrogen isotope signature may be due to secondary processes on parent bodies such as aqueous alteration. Previous work investigated the propensity of PAHs to exchange their hydrogen isotopes with clays, but not in an aqueous environment [7].

Methods: Here, we investigate the hydrogen isotope evolution of phenanthrene and pyrene under aqueous alteration at temperatures comprised between 150 and 350°C. We use perdeuterated, D-rich and poor water solutions ($\delta D = +747‰$ and $-420‰$). We also investigate the impact of a phyllosilicate (saponite) on this process, phyllosilicates being predominant in CM mineralogy [8].

Results: In our first set of experiment, phenanthrene and pyrene efficiently exchanged with perdeuterated water at 150 and 220°C, and reached an equilibrium within a few days, with a value depending on the temperature and the structure of the PAH (pyrene being more enriched than phenanthrene). Then, in a second set of experiment, at the same temperatures but with water at $\delta D = +747‰$, no hydrogen isotope exchange was measured, with the exception of pyrene at 220°C. At 150°C with saponite, no exchange has been measured except for the saponite itself, enriched in deuterium at the end of the experiment. Lastly, we conducted a set of experiments at 350°C with water at $\delta D = +747‰$ and $-420‰$ with and without saponite. PAHs efficiently exchange their hydrogen isotopes with water at this temperature, values reaching a plateau within a week, with a half-life of two days. In the experiments with saponite, exchange rate is increased (half-life of one day) and saponite also efficiently exchange with water. Yet, in this series, the isotope fractionation between PAHs and water is reduced, suggesting that equilibrium is shifted.

Discussion: We show here that at high temperature (350°C) and within a few days, PAHs and water may exchange their hydrogen isotopes. We also show that at temperature representative of alteration in CMs (150°C), PAHs and (perdeuterated) water exchanged their hydrogens in a matter of days. We also see that the structure of the PAHs influences the equilibrium value and that the presence of saponite increases the exchange rate. In natural objects, if the temperature and the duration of alteration events are sufficient, PAHs may have lost their (deuterium-rich) pre-accretional signature as the result of isotope exchange with D-poor water. This is consistent with PAH hydrogen isotope values in CM chondrites decreasing according to the intensity of alteration. Additionally, with other temperature results (330 and 370°C), we will be able to estimate the fractionation and its kinetics at any temperatures and then the duration of aqueous alteration episodes in CM at representative temperatures and the initial values of accreted PAHs on parent bodies.

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