



Transformation of polycyclic aromatic hydrocarbons (PAHs) on Fe(III)-modified clay minerals: Role of molecular chemistry and clay surface properties

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ABSTRACT

Clay-driven transformation of polycyclic aromatic hydrocarbons (PAHs) is critically influenced by their molecular structure and clay surface properties. In the present study, several PAHs were selected as model molecules to investigate their potential transformation on Fe(III)-saturated clay minerals under various mineralogical and environmental conditions. Results suggest that the reactivity of PAHs is highly correlated with their ionization potential (IP) values. PAHs with IP lower than a threshold between 7.5 and 7.6 prefer undergoing a one-electron transfer reaction. Otherwise, Fe(III)-smectite is unable to degrade PAHs with IP above it. The electron-transfer process leads to the reduction of Fe(III) to Fe(II) and formation of organic radical cations, which are more stable in clay interlayers than at other clay sites. Subsequent reactions of radical cations with oxygenic species (such as H₂O) result in formation of oxygenated products. The surface chemical properties, i.e., the hydration of cations, fraction of Fe(III), layer charge location, and type of ligands, strongly affect the interaction between PAHs and Fe(III), thus modulate the reactivity of surface Fe(III)-species on the clay minerals. This study provides the first direct evidence for clay-catalyzed transformation of PAHs supporting the plausibility of their in situ degradation in soils, and demonstrates that abiotic reactions with surface-bound Fe(III) may affect or even dominate the long-term behavior of PAHs in soils, particularly in the presence of swelling clay minerals.

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1. Introduction

Natural phases such as soil and sediment are contaminated with polycyclic aromatic hydrocarbons (PAHs) at levels that are in some instances potentially damaging to human and ecosystem health [1–3]. Ecological impacts and detoxification of those organic contaminants are correlated with their spontaneous biotic and/or abiotic transformation processes under natural conditions [4,5]. Although natural biodegradation has been considered as crucial for PAHs fate in soil, abiotic transformation of PAHs has got attentions recently. Abiotic degradation of organic contaminants is strongly affected by their interactions with chemically active soil components, such as dissolved organic matter, metal oxides,

and clay minerals [6]. In subsurface soil horizons and aquifer sediments with small amounts of organic matter, clay minerals are of interest due to their significant impact on natural biodegradation, chemical transformation and photochemical processes of involved hazardous substances (including PAHs) [7–10].

Smectite is a representative clay mineral, which generally consists of a center octahedral Al–O sheet sandwiched between two tetrahedral Si–O sheets. The planar aluminosilicate layers typically exist in stacked assemblages, which are often referred to as tactoids. Due to isomorphic substitution in the tetrahedral Si and/or octahedral Al layers, negative charges, embedded in the individual layers in a fixed and isolated distribution, are commonly neutralized by exchangeable hydrated cations that reside at or near the negative-charged sites [11]. This unique property enables it to provide desired active sites for organic pollutants bonding on mineral surfaces, where various chemical processes may occur, including the adsorption and transformation of organic compounds [12–14]. PAHs are rich in delocalized π electrons and thus may interact strongly with electron-deficient or positively

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Table 1
Characteristics of clay minerals used in this study and their relevant reaction rates on anthracene transformation.

Clay mineralogy	Cation exchange capacity (cmol kg ⁻¹)	Surface area (m ² g ⁻¹)	Octahedral charge (%)	Exchangeable iron (%)	Rate constants K_{obs} (d ⁻¹)	Normalized K_{obs} (h ⁻¹ mmol ⁻¹ g)
MMT (Swy-1)	87	82.1	76.5	3.16	0.2894	0.513
MMT (SAz-1)	128	97.4	88	4.95	0.2507	0.284
Saponite (SapCa-2)	97.4	75	~0	3.41	0.2424	0.398
Hectorite (SHCa-1)	67	53.9	~100	3.18	0.3410	0.600
Kaolinite	9.5	8.7	–	0.44	0.0020	0.026
Pyrophyllite	13.5	16.2	–	0.99	0.0068	0.038
Illite	21	89.5	–	1.84	0.0122	0.037

charged species via electron-donor–acceptor interactions [15]. The formation of cation– π interactions between π donor and exchangeable cations has been considered as a crucial factor affecting PAHs retention and transformation on mineral surfaces [12,16–18].

Saturation of various cations on clay surface is expected to modify the structure and physical-chemical properties of the clay surface, and thus influences the interaction between metal ions and organic pollutants [19]. As reported previously, the presence of transition metal ions (such as Cu(II), Fe(III), and Ag(I)) on clay surface facilitates the sorption of PAHs due to their strong cation– π interactions [20]. Metal ions such as Fe(III) and Cu(II) ions can also induce electron-transfer between exchangeable cations and adsorbed aromatic molecules on clay surfaces, which might be followed by further transformation processes including oxidation, dechlorination and polymerization [20–28]. Among commonly found metal ions, Fe(III) associated with clay minerals has been proposed to act as renewable source of redox equivalents in soils and sediments [29]. However, limited work has been done to investigate whether the adsorbed PAHs could also be transformed on Fe(III)-exchanged clay surfaces. In addition, redox reactions of Fe(II)/(III) in clay minerals depend on a variety of mineralogical and environmental factors that make an assessment of Fe redox reactivity very challenging [30]. Those factors include the surface properties of clays, active site location, and chemical natures of molecules [14,31]. Other species such as water and organic ligands could also compete for active sites with organic molecules, and thus influence the catalytic activity of clay surfaces [8]. From this prospect, we hypothesize that the molecular chemistry relevant factors may play an important role on clay-driven transformation of PAHs.

In this work, we demonstrate for the first time the transformation of several PAHs (such as naphthalene, phenanthrene, anthracene, chrysene, pyrene, and benzo[a]pyrene) on clay minerals with various surface physicochemical properties under environmentally relevant conditions. The principal objectives of the work are to (1) reveal the influence of organic molecular structure and clay surface properties on clay-facilitated transformation; (2) probe the role of interactions between PAHs and Fe(III)-smectite composite in their transformation; (3) understand the transformation process and determine products distribution of PAHs; and (4) further gain insight into the mechanisms of PAHs transformation on Fe(III)-clay surface. The obtained results could be of significance in assessing the fate of various PAHs and the reactivity of surface-bound Fe(III) present on different clay mineral surfaces.

2. Experimental

2.1. Chemicals and materials

Reference smectites (montmorillonite (SWy-1 and SAz-1), Saponite, and Hectorite), illite, and pyrophyllite were obtained from the Source Clays Repository of the Clay Minerals Society. These clays were chosen to provide a range of cation exchange

capacity (CEC), surface charge densities, differences in origin of charge deficit, and structure of octahedral sheet (dioctahedral vs trioctahedral) (Table 1).

Anhydrous ferric chloride (FeCl₃), sodium hydroxide (NaOH), hydrochloric acid (HCl, 36–38%), hydrofluoric acid (HF, 48%), perchloric acid (HClO₄, 70%), nitric acid (HNO₃, 68–70%) were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Naphthalene (Nap, 98%), phenanthrene (Phe, 98%), anthracene (Ant, 98%), pyrene (Pyr, 99%) and methanol (HPLC-grade solvent) were purchased from Sigma–Aldrich (Shanghai, China).

2.2. Preparation of PAHs contaminated Fe(III)-clay

The preparation of Fe(III)-saturated clay minerals was carried out by following the method of Arroyo et al. [32]. Briefly, the clay suspension was first titrated to pH 6.8 with 0.5 M sodium acetate buffer (pH 5) to remove carbonate impurities. Clay-sized particles (<2 μ m) were obtained by centrifugation of the clay suspension for 6 min at 600 rpm, and then treated with 0.1 M FeCl₃ solutions for four times. The Fe(III)-saturated clays were washed using Milli-Q water until free of chloride as indicated by a negative test with AgNO₃. Smectite clays saturated by other types of cations (e.g., Na⁺, Al³⁺) were achieved by following the same procedures as described above except the substitution of 0.1 M Fe³⁺ by Na⁺, and Al³⁺. To prepare Fe(III)-smectite with different Fe(III) speciation forms, pH of involved suspension was adjusted to a desired value using 1.0 M HCl or NaOH, and then freeze-dried. The clay samples before and after Fe(III) saturation were digested by the mixture of hydrofluoric acid, nitric acid and perchloric acid at 250 °C for 90 min, and Fe contents were determined using a Perkin-Elmer AAnalysis 400 Atomic Absorption Spectrophotometer (AAS, Norwalk, CT). The reaction mixtures of 0.1 mg/g PAHs contaminated clays were prepared by mixing 1 g of cation-modified clays with 5 mL of various PAHs in methanol solution, in which naphthalene, anthracene, phenanthrene, chrysene, pyrene, and benzo[a]pyrene were, respectively, employed in each sample. Methanol was used as solvent of PAHs to allow its evaporation under ambient conditions.

2.3. Transformation of PAHs on clay surface

The reaction was conducted at room temperature (23 °C). One gram of obtained PAHs-contaminated clay was laid onto a Petri dish, and then placed inside the desiccators without light irradiation to prevent any light-induced chemical reactions. The relative humidity was controlled by the saturated salt solutions in reaction cells. To conduct the anaerobic reactions, this reaction system was transferred into an anaerobic chamber. At pre-selected intervals (such as 1 d, 2 d, 3 d, 4 d, and 5 d), the samples were sacrificed and transferred into 50 mL Teflon centrifuge tubes. The residual PAHs and their products were extracted and analyzed immediately.

Approximately 10 mL of extraction solution (mixture of 5 mL acetone and 5 mL dichloromethane) was added to each centrifuge tube containing specified clay samples. The suspensions were extracted in an ultrasonic bath for half an hour, and then

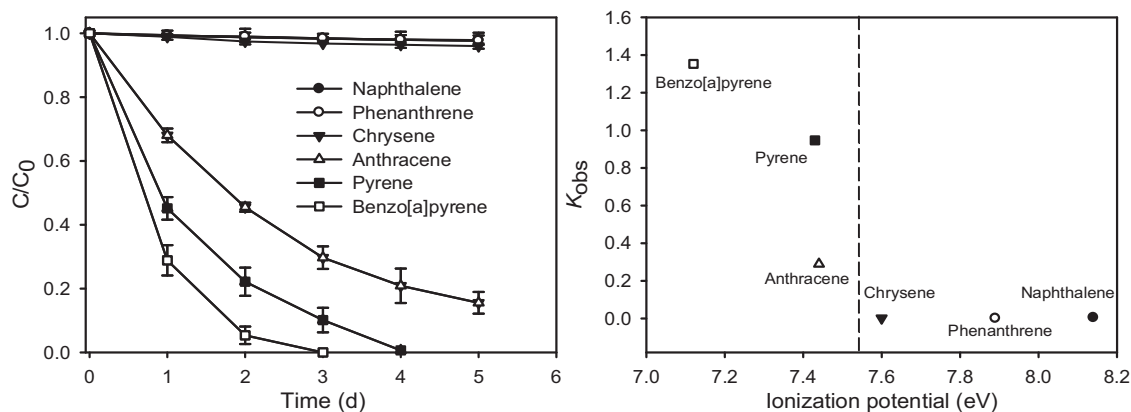


Fig. 1. (a) The evolution of various PAHs as a function of reaction time on Fe(III)-smectite, (b) relationship between the pseudo-first-order rate constant for PAHs degradation and their ionization potential (IP) value.

centrifuged at 10,000 rpm for 10 min to separate the supernatants from the solids. The supernatants were collected and the solid residues were replenished with another 10 mL of extraction solution. Such procedure was repeated twice to assure all the PAHs and their products were extracted. The supernatants were collected together, and filtered using a syringe filter equipped with a 0.22 μm membrane filter. The filtrates were stored in amber HPLC vials, and placed in a refrigerator prior to analysis.

2.4. Detection of PAHs and transformation products

PAHs were quantified using a Thermo Fisher Ultra 3000 HPLC equipped with a 25 cm \times 4.6 mm Cosmosil C18 column. A 85:15 (v/v) mixture of methanol:water was employed as mobile effluent. The flow rate was 1.0 mL min^{-1} , and the ultraviolet detector was set at 254 nm. The PAHs and its intermediate products were identified using a Agilent 7890A-5975C gas chromatograph incorporated with a mass spectrometer operated on a full scan mode (30–500 amu), where a HP-5MS capillary column (length = 30 m; internal diameter = 250 μm ; film thickness = 0.25 μm) was employed. Helium was used as carrier gas at a flow rate of 1.2 mL/min with splitless injection at 230 $^{\circ}\text{C}$. To detect the products of anthracene, the oven temperature was programmed from 80 $^{\circ}\text{C}$ to 200 $^{\circ}\text{C}$ (20 $^{\circ}\text{C min}^{-1}$, 2 min hold), and then to 260 $^{\circ}\text{C}$ (20 $^{\circ}\text{C min}^{-1}$, 2 min hold). For pyrene and benzo[a]pyrene, the oven temperature was programmed from 80 $^{\circ}\text{C}$ to 200 $^{\circ}\text{C}$ (20 $^{\circ}\text{C min}^{-1}$, 2 min hold), then to 260 $^{\circ}\text{C}$ (20 $^{\circ}\text{C min}^{-1}$, 2 min hold), and then to 310 $^{\circ}\text{C}$ (20 $^{\circ}\text{C min}^{-1}$, 2 min hold).

Content of Fe(II) in the reacted system was extracted with water and measured using ferrozine. Briefly, reacted iron-clay suspension was mixed using Vortex for 30 s. Then 0.5 mL of suspension was collected and added to 1 mL of ferrozine solution (100 mM), and the volume of the mixture was adjusted to 15 mL. The suspension was agitated for 2 h and filtered through a 0.45 μm filter. Concentration of ferrozine-complexed Fe(II) was measured by UV-vis spectrophotometer at 562 nm.

3. Results and discussion

3.1. Reaction kinetics of various PAHs on Fe(III)-montmorillonite

Transformation of various PAHs (including naphthalene, phenanthrene, anthracene, chrysene, pyrene, and benzo[a]pyrene) on Fe(III)-montmorillonite clay was, respectively, investigated under relatively dehydrated condition (RH is \sim 8%). The reaction occurs spontaneously, and the brownish color of Fe(III)-montmorillonite samples associated with pyrene

and benzo[a]pyrene changes to gray within couple days. For Fe(III)-montmorillonite clay mixed with other PAHs (such as naphthalene, phenanthrene, anthracene, and chrysene), no noticeable change was observed. Correspondingly, the color of extracts obtained from anthracene, benzo[a]pyrene, and pyrene contaminated clays gradually changes to brownish with the reaction time, while no color changes for samples associated with chrysene, phenanthrene, and naphthalene. Those color changes indicate transformation of the organic compounds via electron transfer in the reaction systems [8,33]. The evolution of PAHs as a function of reaction time is presented in Fig. 1(a). It is noted that almost 30%, 50%, and 70% of anthracene, pyrene and benzo[a]pyrene was transformed in 1 day by Fe(III)-montmorillonite, while insignificant changes in naphthalene, phenanthrene, and chrysene were observed during the experimental period. The reactions generally follow a pseudo-first-order model. Overall, clay-mediated transformation rate follows the order: benzo[a]pyrene > pyrene > anthracene > chrysene \approx phenanthrene \approx naphthalene.

The varied transformation rates for individual PAHs can be ascribed to their physicochemical characteristics such as electronic properties, which can give direct information about their reactivity and stability during transformation processes associated with electron transfer [34,35]. The energy of the highest occupied molecular orbit (HOMO) is considered as one of the basic electronic descriptors, which is roughly related to the ionization potential (or ionization energy) (IP) of a molecule. The correlations between PAHs transformation rates and their IP values (those values are obtained from the National Institute of Standards and Technology (NIST) Chemistry Web Book <http://webbook.nist.gov/chemistry/ion-ser.html>) are shown in Fig. 1(b). It is noted that a threshold of IP for PAHs transformation exists between 7.5 and 7.6. PAHs with IP lower than this value prefer undergoing electron-transfer reaction, while Fe(III)-smectite is unable to degrade compounds with IP above this threshold value. Similar results were observed in other reaction systems. As reported previously, lignin peroxidase and other metabolism processes in cells merely transform PAHs with IP values of <7.55 eV [36,37]. Manganic acetate, on the other hand, was found to be incapable of oxidizing PAHs with IPs equal to or greater than that of chrysene (approximately 7.6 eV) [38]. Those observations are consistent with a mechanism of one-electron oxidation, which is the ability of the tested substrates to form products correlated well with their individual IPs. Based on previous reports (Huckel and Slifkin's theory), the relationship between IP and excited state of PAHs can be expressed with the equation:

$$I = \alpha + bE$$

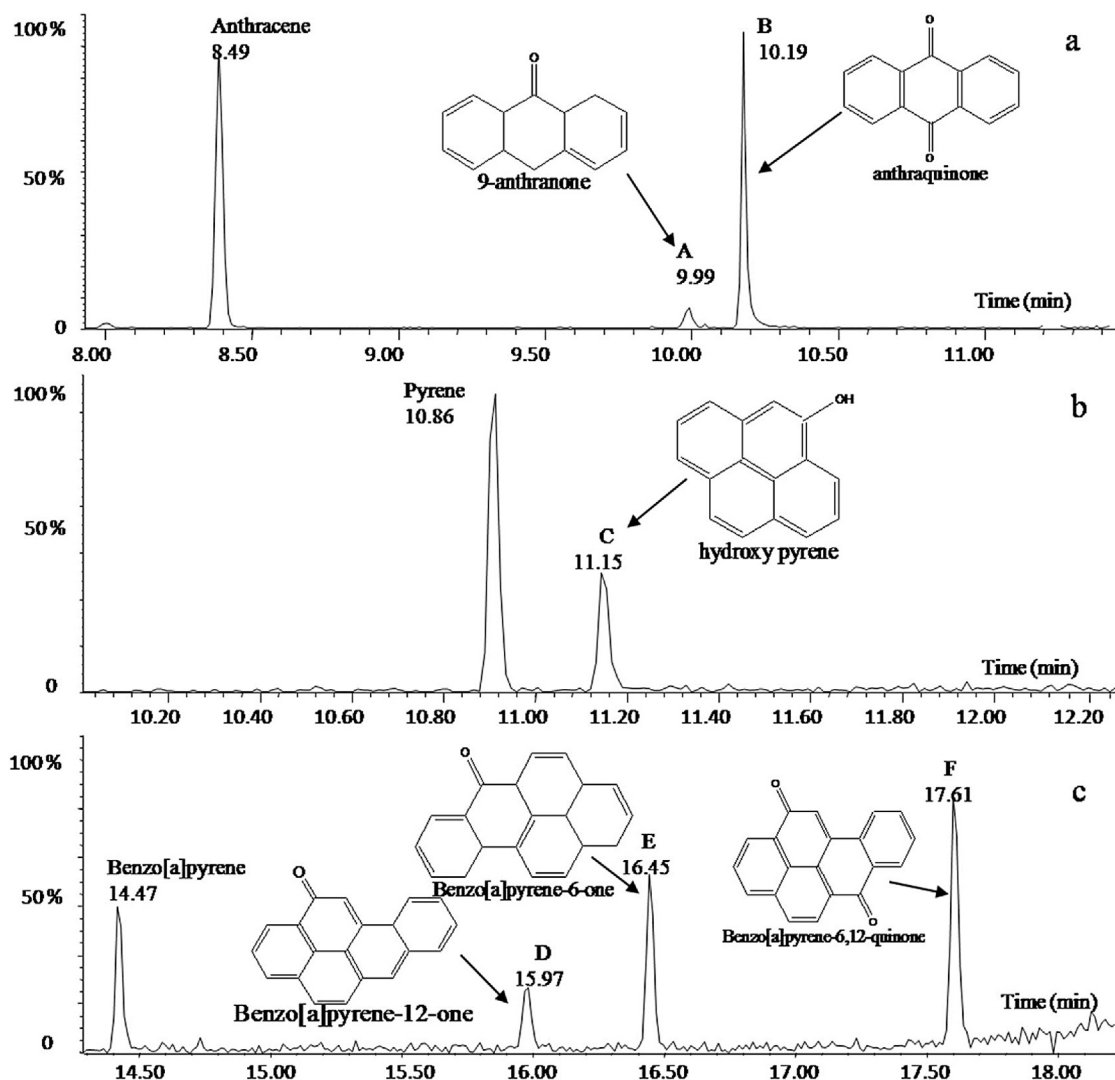


Fig. 2. GC-MS chromatograms of 1:1 acetone/dichloromethane extract of the (a) Fe(III)-montmorillonite/anthracene reaction mixture after 2 h of reaction time, (b) Fe(III)-montmorillonite/pyrene reaction mixture after 0.5 h of reaction time, and (c) Fe(III)-montmorillonite/benzo[a]pyrene reaction mixture after 1 h of reaction time.

where I denotes the IP of PAHs molecules, E is the energy of excited state, and α corresponds to threshold IP value of PAHs that can be excited by electron-acceptor species. This value might be variable with the oxidation capability of an oxidizing agent. Generally, PAHs with lower IP are characterized by higher charge transfer, thus being easier to undergo a definite one-electron transfer reaction and oxidized by the interlayer transition-metal ions [27]. Compared to phenanthrene and naphthalene, pyrene (or anthracene) has lower IP value and higher electron-donating capacity, and is thereby easier to act as an electron-donor to interact with Fe(III). This makes pyrene and anthracene have a strong tendency to form radical cations, thus induce the further transformation and oxidation products [39]. In other systems, the transformation rate of organic molecules with conjugated π -system was found to be linearly correlated with their IP [40]. For example, the values for the percent recoveries of most of the PAHs compounds with IP value between 7.2 and 8.1 eV correlated very well with their IPs in manganese peroxidase-mediated lipid peroxidation reactions [41]. However, no significant correlation was found between oxidation rate and IP value of transformable PAHs (such as pyrene, anthracene, and benzo[a]pyrene) in the present study. For example, pyrene was more degradable than anthracene on Fe(III)-smectite although both compounds have a similar IP (7.44 vs. 7.43 eV). This indicates that PAHs transformation in Fe(III)-smectite catalyzed

processes is more complicated and the transformation rate of PAHs not merely depends on their IP value.

3.2. Reaction products of PAHs on Fe(III)-montmorillonite

Major transformation products of anthracene, pyrene, and benzo[a]pyrene were obtained by extraction of the reaction samples with 1:1 acetone/methylene dichloride and were identified by GC-MS analysis. Fig. 2 displays the GC-MS chromatograms of those compounds and the corresponding transformation products related to GC peaks. The main transformation products of anthracene could be identified as anthraquinone, formed by ketonizing the intermediate benzene ring of anthracene. It is noted that anthranone can be considered as a major detectable intermediate for the transformation from anthracene to anthraquinone. For cation-anthracene complexes, the metal ion bounds symmetrically to the parent system, giving lower interaction energy than the ones that bounds asymmetrically. This complexation increases the electron density of carbon atoms located at the central ring of anthracene, and consequently the electron density of carbon atoms on the central C6-ring is higher than that of outer rings [42–44]. Therefore, the carbon located on the central ring tends to be oxidized compared to others, and 9,10-anthraquinone is

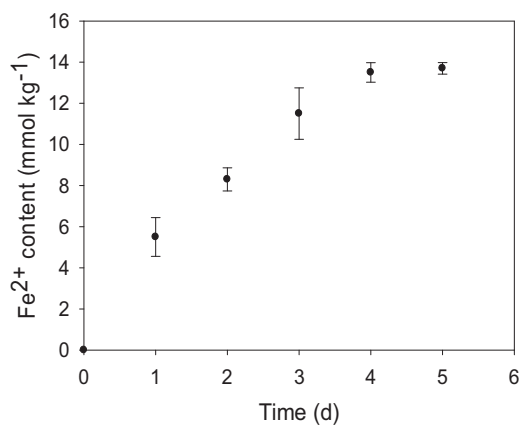


Fig. 3. The evolution of Fe²⁺ as a function of reaction time in the reaction system of anthracene transformation on Fe(III)-smectite.

readily formed during the transformation of anthracene by the Fe(III)-modified clay. Similar with anthracene, the final transformation product of benzo[a]pyrene is benzo[a]pyrene-6,9-quinone, accompanying with benzo[a]pyrene-6-one and benzo[a]pyrene-9-one as intermediates. As described previously, anthraquinone and benzo[a]pyrene-quinone were also identified as the principal products during micro-biological degradation oxidation of anthracene and benzo[a]pyrene [34,45]. On the other hand, 1-hydroxypyrene is detected as the main product of pyrene. Therefore, the products formation was found to be structure dependent. Radical cations localized at L-regions, such as those formed from anthracene and benz[a]anthracene, react preferentially with H₂O or/and O₂ to produce quinines as primary products, whereas radical cations generated from hydrocarbons without an L-region, such as pyrene typically react with H₂O to form hydrolyzed derivatives as primary products.

3.3. Reactivity sites for PAHs transformation

Transformation of PAHs not only depends on their organic molecular structure but also the oxidization power of the interlayer metal ions. Only metal ions with suitable oxidization power such Fe(III), Cu(II), and Ru(III) ions can induce the electron-transfer and make the subsequent reactions possible. In this study, electron-accepting sites in clay minerals are considered to be derived from the interlayer transition-metal ions (i.e., exchangeable Fe(III)). This is supported by the increasing Fe(II) concentration on Fe(III)-montmorillonite with reaction time (Fig. 3). In addition to the Lewis acid character of the Fe(III)-montmorillonite, the hydrated cation-exchanged montmorillonites (such as Al(III)-smectite and Fe(III)-smectite) act as strong Bronsted acids, where the reactive protons are derived from the dissociation of hydrated water molecules because of polarization by exchangeable cations. This type of active site is also effective on the transformation of certain organic molecules such as organophosphorus pesticides [27]. However, the presence of Al(III) on clay surface exhibits insignificant effect on PAHs transformation (Fig. 4). This confirms that the transformation of PAHs is mainly due to the Lewis-acid sites (electron-accepting sites) derived from the transition-metal ions (such as Fe(III)) on clay minerals in this reaction system.

3.4. Reactivity sites of different clay

Fe(III) located on different mineral sites exhibits various reactivities with contaminants. Three different types of exchangeable Fe(III) species can be found on clay minerals simultaneously, i.e.,

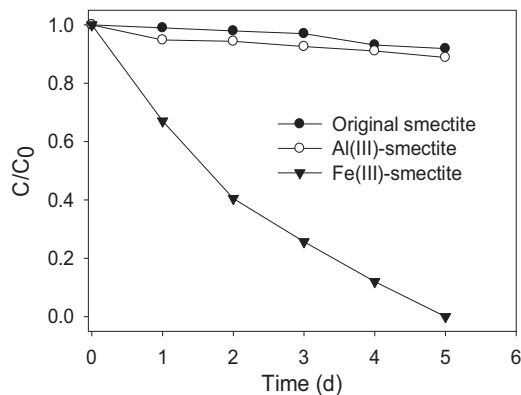


Fig. 4. The evolution of anthracene as a function of reaction time at smectite modified by various cations.

Fe(III) complexed by hydroxyl groups at edge surfaces, Fe(III) within the clay interlayers, and Fe(III) bound by ion exchange at external basal siloxane surfaces. To compare the relative reactivities of those Fe(III) species, transformation of anthracene on three types of Fe(III)-saturated 2:1 structural clays such as pyrophyllite, illite, and montmorillonite were investigated. As displayed in Table 1, the exchangeable iron contents were ca. 3.16%, 1.84%, and 0.99% for Fe(III)-saturated montmorillonite, illite, and pyrophyllite, respectively. This order is consistent with the order of cation exchange capacity (CEC) values of the clays. Montmorillonite possesses the greatest CEC, and is expandable clay with accessible cation exchange sites present in the interlayers as well as on the external surfaces of the stacked layer assemblages. Pyrophyllite clay has essentially no isomorphous substitution and the small amount of negative charges result mostly from the dissociation of hydroxides at edge sites, hence a small quantity of exchangeable Fe resides primarily on the edge sites. For illite, though it possesses high surface negative-charged density on clay layers, most of structural charges originating from isomorphous substitution in clay interlayers are compensated by fixed K⁺ which cannot be replaced by the added Fe(III), thus exchangeable Fe(III) ions are mainly located on external surfaces. Therefore, anthracene transformation on Fe(III)-saturated pyrophyllite was conducted to examine the reactivity of Fe(III) bound on edge surfaces, while illite was used to reflect the reactivity of Fe(III) bound by surface complexes to hydroxyl groups and by ion exchange on external surfaces. Compared with pyrophyllite and illite, Fe(III) located on montmorillonite could refer to the reactive sites in clay interlayers.

In dealing with the reactivity of Fe(III) bound to the mineral surfaces, observed rate constants are normalized to the content of surface-bound Fe(III), which reflect different intrinsic reactivities of various active sites in the clay minerals [46]. As shown in Table 1, the transformation rates normalized to the content of reactive Fe(III) sites are 0.513, 0.037, and 0.038 mmol⁻¹ g in the cases of Fe(III)-montmorillonite, Fe(III)-illite, and Fe(III)-pyrophyllite, respectively. The reactivity of Fe(III) adsorbed on montmorillonite is about 10 times higher than that on illite and pyrophyllite clays. This indicates that Fe(III) located in the clay interlayers exhibits the highest reactivity among the reactive Fe(III) sites on clay surfaces, in agreement with what reported previously [47]. On the other hand, the comparatively low reactivity of pyrophyllite and illite suggests that Fe(III) ions on external surface and clay edge sites play only a minor role in anthracene transformation. This can be attributed to the stabilization effects of the planar montmorillonite clay interlayers for organic radicals [8,44]. During the PAHs transformation process, the electron-transfer reaction could induce the formation of organic radical cations, which are more stable in clay interlayer than in outer spaces [8,44]. Therefore, montmorillonite

Table 2
Transformation rate constant (k_{obs}) of PAHs on Fe(III)–smectite surface with various physicochemical parameters.

PAHs	Relative humidity (%)	Iron (III) fraction (%)	Organic ligands	Atmosphere	k_{obs}
Naphthalene	8	100	None	Oxic	~0
Phenanthrene	8	100	None	Oxic	~0
Chrysene	8	100	None	Oxic	~0
Pyrene	8	100	None	Oxic	0.9466
Benzo[a]pyrene	8	100	None	Oxic	1.3524
Anthracene	8	100	None	Oxic	0.2894
Anthracene	11	100	None	Oxic	0.3117
Anthracene	30	100	None	Oxic	0.2073
Anthracene	60	100	None	Oxic	0.1425
Anthracene	90	100	None	Oxic	0.0814
Anthracene	8	90	None	Oxic	0.2547
Anthracene	8	50	None	Oxic	0.1502
Anthracene	8	10	None	Oxic	0.0314
Anthracene	8	100	Oxalate acid	Oxic	0.0145
Anthracene	8	100	Citric acid	Oxic	0.0295
Anthracene	8	100	EDTA	Oxic	0.0083
Anthracene	8	100	None	Anoxic	0.2885

with significant amount of interlayer surface areas exhibits the highest reactivity than other tested clays.

3.5. Reactivity of various smectite

The location and amount of isomorphous substitution in clay sheets also influences the interactions between PAHs and cations and hence the transformation of PAHs [20,31]. Smectite clays with different lattice charge distribution (i.e., saponite, montmorillonite, and hectorite) saturated with Fe(III) were chosen, and anthracene transformation rates on those clays are presented in Table 1. As shown in Table 1, Fe(III)–hectorite is the most effective in promoting anthracene transformation, followed by Fe(III)–montmorillonite and Fe(III)–saponite. The isomorphous substitution of montmorillonite is mainly derived from octahedral (Mg^{2+} for Al^{3+}) substitution along with a small quantity of tetrahedron (Al^{3+} for Si^{4+}), and hectorite is a trioctahedral smectite entirely substituted in the octahedral layer (Li^+ for Mg^{2+}) where charge deficit originates in the octahedral layer. For saponite, the negative charge deficit originates primarily from isomorphous substitution of Si^{4+} by Al^{3+} , which results in the distribution of negative charges in tetrahedral layers [48]. Therefore, the isomorphous substitution of hectorite and montmorillonite occurs in the central octahedral layer resulting in the negative charges being distributed over more oxygen atoms on both sides of the 2:1 clay layers, but with a smaller portion of negative charge associated with each oxygen atom. The more distributed structural charge on montmorillonite surfaces suggests comparatively weak interactions with exchangeable cations as evidenced by the formation of fully hydrated outer-sphere complexes [49]. Due to tetrahedral layer isomorphous substitution, saponite develops relatively strong interactions with inorganic exchangeable cations such as Fe(III) involving formation of inner-sphere complexes [49,50]. This stronger binding of Fe^{3+} to the smectite surface is related to the weaker affinity of anthracene to montmorillonite in the position P_{oct} than in the position P_{tet} reversely. Therefore, smectite clays with a lower tetrahedral charge (such as hectorite and montmorillonite) are more favorable for the interaction between cation and anthracene, which is a requisite for electron transfer and anthracene transformation.

In addition, the variation in the reactivity of different clay sites is also related with surface densities of reactive Fe(III) [12,46]. Among the investigated smectites, SAz-1 (montmorillonite) has the highest CEC (and surface charge density) resulting in a larger number of cations per unit cell (as shown in Table 1). However, crowding interlayer cations may increase the electrostatic repulsion among

these cations, thereby contributing to the reduction of pollutants adsorption by more highly charged clay [12]. On the other hand, the lower charged clay apparently has larger exposed areas between the neutral siloxane surfaces, which contribute more exchangeable cations on favorable PAHs adsorptive domains. Thus, SAz-1 exhibits lower reactivity for anthracene transformation than SWy-1 clay. These results suggest that for anthracene transformation, the CEC of the swelling clays is not the limiting factor.

3.6. Influence of surface physicochemical parameters

To investigate the influence of clay surface properties and environmental factors on transformation rate of PAHs, kinetic experiments were conducted under various experimental conditions such as relative humidity (RH), Fe species, organic ligands, and reaction atmosphere. As shown in Table 2, the increase in the moisture content that ranges from 8% to 11% leads to a small amount of improvement in anthracene transformation. This might be due to that the ligand water molecules around exchangeable cation participate in the transformation reaction. Further increase in RH above this percentage results in a steep decrease in the transformation rate. When RH is 90%, the transformation of anthracene on clay surfaces is almost completely retarded. This result is in agreement with previous reports, in which the addition of water to a system associated with arene transformation on silica–alumina resulted in a rapid decay of reaction rate [51]. The suppress effect by water is attributed to a competition between arene and water molecule for the Lewis acid site (such as Fe(III) on clay surfaces) [51]. Generally, cations on clay surface tend to be hydrated, resulting in the formation of water layer in interfacial region [14]. The coverage of water molecules leads to an increasing detachment of anthracene from the inner-sphere coordination sites of cations. Thus, the hydration status of smectite clay interlayers appears to be an important factor influencing the interaction between cation and organic contaminants, which is controlled by the size of hydrated exchangeable cations and the distance between the positive- and negative-charged centers [20]. Meanwhile, the decreasing anthracene–Fe(III) interaction on clay surface induces the decrease in electron transfer reaction rate and PAHs transformation rate on clay surface [44]. On the other hand, dehydration of Fe(III)–smectite enhances PAHs chemisorptions, which, in turn, allows the reaction of electron transfer [24]. Therefore, the presence of free water blocks the active sites and hinders the catalytic effect of the clay surface; the interlayer water must be removed to certain extent for the oxidative reaction of organic molecules to proceed.

In natural soil environment, Fe(III) on clay surfaces may form small oligomers such as $[\text{Fe}(\text{OH})_{1-4}]_n^{-1-2+}$ and $\text{Fe}_x(\text{organic ligands})_y^{n+}$, combining with OH^- and/or organic ligands. Those complexes could exhibit distinct properties for electron-donation or interaction with organic molecules. However, the organic compound should assume a direct ligand position with the metal cation for the electron-transfer reaction occurring [24]. It is hypothesized that the exchangeable Fe(III) ions forming inert species such as polymeric iron hydroxides might reduce the oxidation potential of the metal ion or hinder the access of the PAHs molecules to the metal ion positions, inducing the decrease of PAHs transformation on the clay surface. To test this hypothesis, Fe(III)-saturated montmorillonite samples were aged under various pH conditions, and the Fe(III) fraction was calculated based on the theoretical Fe(III) species-pH relationship. The reactivity of Fe(III)-montmorillonite samples with various Fe(III) fractions was evaluated by anthracene transformation. As shown in Table 2, the k_{obs} value is 0.2547 h^{-1} when Fe(III) fraction is 90%, and it rapidly decreases to 0.0314 h^{-1} when decreasing the Fe(III) fraction value to 10%. Thus, the disappearance of anthracene is correlated with Fe(III) species, indicating that the PAHs transformation is mainly owing to the electron transfer from aromatic ring to electron-acceptor such as Fe(III) on clay surface. On the other hand, the presence of organic ligands (such as oxalate, citric acid, and EDTA) also suppresses the transformation of anthracene on clay surface. Organic ligands with higher affinity such as EDTA show greater restraining effect on transformation rate than other lower affinity molecular ligands. This suggests that strong complexation between Fe(III) and organic ligands may hinder the access of the PAHs molecules to the metal ion positions, thus inhibiting the electron transfer and radical formation. Similarly, the presence of soil organic matter also decreases the transformation of organic compounds due to the decreased number of active sites available at the clay surfaces [52]. These results indicate that the direct coordination of organic molecules to metal ions ensures the electron transfer and further transformation for organic contaminants [24].

In some oxidation reactions, such as those of aromatic amines and phenols, oxygen assists in the formation of radicals (cations), even in the absence of transition metal ions [27]. Moreover, the formed aromatic radicals could also be oxidized by the adsorbed oxygen [27]. In the present study, the transformation process of PAHs involves the carbonylation and hydroxylation of parent compounds, indicating that the oxygenic species participate in the oxidative reaction. To investigate the potential role of oxygen, the anthracene transformation reaction was conducted under anoxic conditions. As shown in Table 2, the absence of oxygen has no influence on anthracene transformation rate, indicating that oxygen may not participate in the oxidative reaction. Besides oxygen, other species such as H_2O , anions and organic molecular might also be incorporated into the reaction products [53]. For example, the presence of water molecules during the equilibration of benzene with the partially hydrated clay film may have contributed to the formation of bands attributable to oxygen and/or hydrogen containing surface species [54].

3.7. Mechanism

Based on the results above, the reaction pathways of PAHs abiotic transformation oxidation by Fe(III)-montmorillonite are likely to be accomplished by several stages of electron-exchange reactions. First of all, one electron is initially transferred from a π orbital of adsorbed PAHs to the nonbonding orbital of the iron center, thereby resulting in the formation of cation- π complexes on clay surfaces (as shown in Fig. 5). This process decreases the electron density of the PAHs and induces the formation of organic radical cations. Meanwhile, the iron is reduced from Fe(III) to

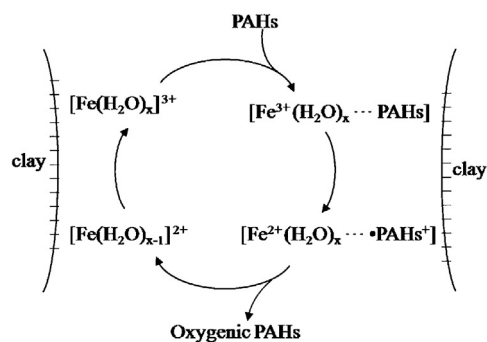


Fig. 5. Proposed mechanism for the transformation of PAHs on Fe(III)-modified clay.

Fe(II). Finally, the reaction of radical cation intermediates with oxygenic species such as H_2O results in the formation of products containing additional oxygen atoms (such as PAH-quinones or PAH-hydroxyls) [8,28,51]. While, Fe(II) on smectite clay can be easily oxidized to Fe(III), which could undergo another catalytic cycle. The key role of montmorillonite, in addition to providing the necessary Fe(III)/Fe(II) couple and acting as microreactor for electron-transfer reaction, is apparently to stabilize the reactive radical cation intermediate [51]. Comparatively, hydrated transition metal ions in aqueous solution are incapable of inducing the electron transfer so that the radical cation species is not formed, indicating the unique role played by the planar silicate surface [55].

4. Conclusions

The present work demonstrates the plausibility of PAHs transformation on the surfaces of natural smectite clays under environmentally relevant conditions. Those transformations greatly depend on the chemical properties of the PAHs. The PAHs with up to four rings (such as benzo[a]pyrene and pyrene) that have low IP values are readily transformed on Fe(III) saturated clay minerals. The products, such as PAH-quinones, usually have higher solubility and enhanced biological activity than their parent compounds. This abiotic transformation of PAHs may represent the first step in the sequence of events leading to the observed biological activity of the hydrocarbon. This raises the possibility that clay-based systems such as transition-metal ion saturated smectite may be used as a new type of materials in the contaminated soil or other subsurface. Advantages of this system are that Fe(III)-smectite is easily prepared from inexpensive natural materials such as smectite minerals, and the reaction temperature is quite moderate. Thus, there is great potential, in developing techniques of Fe(III)-modified clay for treatment of the PAHs contaminated field, altering their environmental toxicity and bioavailability and accelerating the pace of in-situ and ex-situ remediation.

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References

- [1] P.L. Xiaojun Li, Xin Lin, Chungui Zhang, Qi Li, Zongqiang Gong, *J. Hazard. Mater.* 150 (2008) 21–26.
- [2] R.N. Albert, L. Juhasz, *Int. Biodeterior. Biodegrad.* 45 (2000) 57–88.
- [3] O.V.S.a.R.K.J. Sudip, K. Samanta, *Trends Biotechnol.* 20 (2002) 243–248.
- [4] K.C. Sorensen, J.W. Stucki, R.E. Warner, M.J. Plewa, *Environ. Sci. Technol.* 38 (2004) 4383–4389.
- [5] S. Gan, E.V. Lau, H.K. Ng, *J. Hazard. Mater.* 172 (2009) 532–549.
- [6] S.A. Boyd, G.Y. Sheng, B.J. Teppen, C.J. Johnston, *Environ. Sci. Technol.* 35 (2001) 4227–4234.
- [7] H.Z. Jia, J.C. Zhao, X.Y. Fan, K. Dilimulati, C.Y. Wang, *Appl. Catal. B: Environ.* 123 (2012) 43–51.
- [8] C. Gu, H. Li, B.J. Teppen, S.A. Boyd, *Environ. Sci. Technol.* 42 (2008) 4758–4763.
- [9] M. Kowalska, D.L. Cocke, *Clay Clay Miner.* 40 (1992) 237–239.
- [10] F. Ounnas, S. Jurjan, M.A. Dziurla, Y. Guivarç'h, C. Feidt, G. Rychen, *Chemosphere* 77 (2009) 115–122.
- [11] C. Gu, H.Z. Jia, H. Li, B.J. Teppen, S.A. Boyd, *Environ. Sci. Technol.* 44 (2010) 4258–4263.
- [12] W.H. Zhang, L.W. Zhuang, Y.A. Yuan, L.Z. Tong, D.C.W. Tsang, *Chemosphere* 83 (2011) 302–310.
- [13] L. Xiao, X.L. Qu, D.Q. Zhu, *Environ. Sci. Technol.* 41 (2007) 2750–2755.
- [14] S. Tamamura, T. Sato, Y. Ota, N. Tang, K. Hayakawa, *Acta Geol. Sin. Engl.* 80 (2006) 185–191.
- [15] X. Qu, P. Liu, D. Zhu, *Environ. Sci. Technol.* 42 (2008) 1109–1116.
- [16] K.U. Goss, R.P. Schwarzenbach, *Environ. Sci. Technol.* 35 (2001) 1–9.
- [17] G.W. Gokel, L.J. Barbour, S.L. De Wall, E.S. Meadows, *Coord. Chem. Rev.* 222 (2001) 127–154.
- [18] X.L. Qu, P. Liu, D.Q. Zhu, *Environ. Sci. Technol.* 42 (2008) 1109–1116.
- [19] W. Zhang, L. Zhuang, Y. Yuan, L. Tong, D.C. Tsang, *Chemosphere* 83 (2011) 302–310.
- [20] D. Zhu, B.E. Herbert, M.A. Schlautman, E.R. Carraway, J. Hur, *J. Environ. Qual.* 33 (2004) 1322–1330.
- [21] S.A. Boyd, M.M. Mortland, *Environ. Sci. Technol.* 20 (1986) 1056–1058.
- [22] N. Govindaraj, M.M. Mortland, S.A. Boyd, *Environ. Sci. Technol.* 21 (1987) 1119–1123.
- [23] C.T. Johnston, T. Tipton, D.A. Stone, C. Erickson, S.L. Trabue, *Langmuir* 7 (1991) 289–296.
- [24] C.T. Johnston, T. Tipton, S.L. Trabue, C. Erickson, D.A. Stone, *Environ. Sci. Technol.* 26 (1992) 382–390.
- [25] E. Wloch, B. Sulikowski, R. Dula, E.M. Serwicka, *Colloid Surf. A* 115 (1996) 257–265.
- [26] M.M. Mortland, L.J. Halloran, *Soil Sci. Soc. Am. J.* 40 (1976) 367–370.
- [27] Y. Soma, M. Soma, *Environ. Health Perspect.* 83 (1989) 205–214.
- [28] C. Liyanapatirana, S.R. Gwaltney, K. Xia, *Environ. Sci. Technol.* 44 (2010) 668–674.
- [29] V. Ernsten, W.P. Gates, J.W. Stucki, *J. Environ. Qual.* 27 (1998) 761–766.
- [30] A. Neumann, S. Petit, T.B. Hofstetter, *Geochim. Cosmochim. Acta* 75 (2011) 2336–2355.
- [31] L. Calamai, O. Pantani, A. Pusino, C. Gessa, P. Fusi, *Clay Clay Miner.* 45 (1997) 23–27.
- [32] L.J. Arroyo, H. Li, B.J. Teppen, S.A. Boyd, *Clay Clay Miner.* 53 (2005) 511–519.
- [33] S.A. Boyd, M.M. Mortland, *Nature* 316 (1985) 532–535.
- [34] P.J. Collins, M. Kotterman, J.A. Field, A. Dobson, *Appl. Environ. Microbiol.* 62 (1996) 4563–4567.
- [35] A. Majcherczyk, C. Johannes, A. Huttermann, *Enzyme Microb. Technol.* 22 (1998) 335–341.
- [36] K.E. Hammel, B. Kalyanaraman, T.K. Kirk, *J. Biol. Chem.* 261 (1986) 6948–6952.
- [37] A.F. Lehner, J. Horn, J.W. Flesher, *Biochem. Biophys. Res. Commun.* 322 (2004) 1018–1023.
- [38] E. Cavalieri, E. Rogan, *Environ. Health Perspect.* 64 (1985) 69–84.
- [39] S. Tobita, S. Leach, H.W. Jochims, E. Ruhl, E. Illenberger, H. Baumgartel, *Can. J. Phys.* 72 (1994) 1060–1069.
- [40] X. Wu, A.P. Davis, P.C. Lambert, L.K. Steffen, O. Toy, A.J. Fry, *Tetrahedron* 65 (2009) 2408–2414.
- [41] B.W. Bogan, R.T. Lamar, *Appl. Environ. Microbiol.* 61 (1995) 2631–2635.
- [42] S. Ikuta, *J. Mol. Struct.-Theochem* 530 (2000) 201–207.
- [43] D. Vijay, G.N. Sastry, *Phys. Chem. Chem. Phys.* 10 (2008) 582–590.
- [44] C. Gu, C. Liu, Y.J. Ding, H. Li, B.J. Teppen, C.T. Johnston, S.A. Boyd, *Environ. Sci. Technol.* 45 (2011) 3445–3451.
- [45] J. Fried, D.E. Schumm, *J. Am. Chem. Soc.* 89 (1967) 5508–5509.
- [46] M. Elsner, R.P. Schwarzenbach, S.B. Haderlein, *Environ. Sci. Technol.* 38 (2004) 799–807.
- [47] Y.B. Si, S.Q. Wang, D.M. Zhou, H.M. Chen, *Clay Clay Miner.* 52 (2004) 742–748.
- [48] W.F. Bleam, *Clay Clay Miner.* 38 (1990) 527–536.
- [49] G.S. Jeffery Greathouse, *J. Phys. Chem. B* 102 (1998) 2406–2414.
- [50] G. Sposito, R. Prost, *Chem. Rev.* 82 (1982) 553–573.
- [51] J.P. Rupert, *J. Phys. Chem.* 77 (1973) 784–790.
- [52] M.M. Elamamy, T. Mill, *Clay Clay Miner.* 32 (1984) 67–73.
- [53] M.P. Eastman, D.E. Patterson, K.H. Pannell, *Clay Clay Miner.* 32 (1984) 327–333.
- [54] P. Kovacic, M.B. Jones, *Chem. Rev.* 87 (1987) 357–379.
- [55] T. Polubesova, S. Eldad, B. Chefetz, *Environ. Sci. Technol.* 44 (2010) 4203–4209.