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Facilitating Effects of Metal Cations on Phenanthrene Sorption in Soils

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Effects of metal cations (Na^+ , Ca^{2+} , and Al^{3+}) on phenanthrene sorption were investigated using two soils with contrasting organic carbon (OC) contents. The presence of the polyvalent cations (i.e., Ca^{2+} or Al^{3+}) at a concentration of 0.01 mol/L significantly increased the capacity and nonlinearity of phenanthrene sorption to soils compared with the monovalent Na^+ . The effects were governed by the content of soil OC. Rubbery OC (i.e., soft, amorphous OC including dissolved organic carbon (DOC)) tended to become condensed on soil surfaces as evidenced by a decrease in the signals of the ^1H NMR spectra of DOC and an increase in the glass transition temperature (T_g) of the soils when the polyvalent cations were present. Increasing Ca^{2+} concentration led initially to an effect similar to that of the polyvalent cations in the low cation concentration range, and the effect was gradually attenuated as Ca^{2+} concentration further increased. These findings lead us to propose that the modifications in the physical configuration and chemical characteristics of OC resulting from the presence of metal cations account for the increase in the capacity and nonlinearity of phenanthrene sorption to the soils. This study points to an important role of metal cations in the sorption and fate of phenanthrene in the soil environment.

Introduction

Soil organic carbon (OC) plays a dominant role in the sorption of polycyclic aromatic hydrocarbons (PAHs) in the environment (1–4). Although the exact mechanism involved still remains unclear, it is well-accepted that the sorption of PAHs in a soil–water system is governed by a mechanism of the dual reactive domain model which proposes that OC comprises two important heterogeneous sorption domains: a “rubbery”, soft, or amorphous domain and a “glassy”, hard, or condensed domain depending on its structure and molecular weight (5–8). Organic carbon in soils may contain a mixture of these particles, or individual particles may contain microdomains that vary widely in glassy character.

Organic carbon may exhibit different sorption characteristic for PAHs depending on its rigidity (2, 8). Sorption in rubbery carbon occurs by solid-phase dissolution and generates isotherms that are linear and noncompetitive, while sorption in glassy carbon occurs by a dual mechanism that includes dissolution and hole-filling processes, exhibiting a nonlinear and competitive sorption character. The glassy status of OC is not constant and can be affected by environmental factors such as heavy metals. It has been reported that in the presence of metal cations humic acids and biopolymers become more condensed in structure and exhibit higher rigidity as evidenced by the glass transition temperature (T_g) (9, 10). In spite of its potential importance, very few direct studies have been conducted to clarify the effect of heavy metals on sorption of organic contaminants. Changes in the structure of OC and the consequent influence on PAH sorption caused by the presence of heavy metals have been observed by using humic acids as sorbents (10). However, the effect of metal cations on changes in soil OC and PAH sorption and the mechanisms involved have not been adequately investigated in soils due to the complexity of soil structure and composition.

Studies have indicated that physical conformation and chemical characteristics of OC at the solid–aqueous interface are important in governing PAH sorption (11). Coagulation of OC has been demonstrated to decrease the sorption of PAHs (12–14). However, several studies have also claimed that condensed OC exhibits greater sorption capacity and nonlinearity for PAHs (9, 10, 15). We therefore hypothesize that metal cations may exert their influence on the sorption of PAHs to soil via changes in the physical configuration and chemical characteristics of soil OC. We have therefore used spectroscopic and microscopic investigation in an attempt to examine such effects in detail and to explore the mechanisms involved.

The origin and diagenetic history of OC in soils may also exhibit significant effects on PAH sorption depending on the content and composition of the OC (1, 8). In the present study two soils with different OC contents and phenanthrene, a model PAH contaminant, were selected as sorbents and sorbate. We used Na^+ , Ca^{2+} , and Al^{3+} , abundant in the soil environment, as examples of metal cations that were expected to exert different effects on sorption because of their different valences. The specific objectives of the study were therefore (i) to chemically characterize the soil properties in the presence of Na^+ , Ca^{2+} , or Al^{3+} , (ii) to quantify the effects of the various cations on the sorption of phenanthrene by soils with different OC content, and (iii) to elucidate the mechanisms involved in the effects of cation concentration on phenanthrene sorption by the soils.

Materials and Methods

Sorbents. Two contrasting soils with different clay mineral and OC contents were used. A black chernozem soil (a clay loam Mollisol) was collected from Heilongjiang Province, northeastern China, and a red soil (a clay Ultisol) from Jiangxi Province, southern China. The original soils had pH values (soil:water, 1:5 (w/v)) of 6.5 and 5.1 and OC contents of 3.94 and 0.66% (0–25 cm depth), and the main clay minerals were smectite and kaolinite in the black soil and red soil, respectively. Soil samples obtained by the following two treatments were used as the sorbents. The soils were extracted with 0.005 mol/L NaCl (soil:solution, 1:50 (w/v)) for 6 h at least 4 consecutive times to remove DOC and then centrifuged at 7200g for 30 min. The residues were collected and freeze-

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TABLE 1. DOC Contents, Thermodynamic Properties, Surface Areas, And ζ Potentials of the Soil Samples As Affected by Metal Cations^a and DOC Removal

soil sample	DOC (mg/kg)	T_g (°C)	N ₂ BET SA (m ² /g)	av pore diam (nm)	ζ potential (mV)
black soil—original	852 ^b	64.1 ^c	30.9 ^d	3.8	−29.6
Na ⁺ treated	865	64.8	31.0	3.7	−24.2
Ca ²⁺ treated	485	66.6	28.1	4.2	−12.7
Al ³⁺ treated	446	69.7	27.7	4.4	−8.5
DOC removed	98	67.5	32.8	3.6	−21.9
roasted at 375 °C	^e		69.8	3.2	
red soil—original	298	60.4	40.6	8.1	−18.8
Na ⁺ treated	289	61.1	41.3	8.4	−17.6
Ca ²⁺ treated	174	64.5	37.2	9.3	−7.4
Al ³⁺ treated	152	65.2	36.4	9.6	−6.9
DOC removed	26	64.3	42.3	8.7	−16.2
roasted at 375 °C			55.4	7.6	

^a Cation (Na⁺, Ca²⁺, Al³⁺) concentration used was 0.01 mol/L. ^b DOC removed by 0.005 mol/L NaCl at least 4 times for 6 h each time; DOC in the original soil samples and DOC depleted samples were extracted with 0.005 mol/L NaCl for 6 h. ^c T_g is the calculated glass transition temperature. ^d N₂ BET SA is the cumulative surface area of pores between 1.7 and 300 nm in diameter determined with N₂ at 77 K using the Brunauer–Emmett–Teller equation. ^e Blank indicates zero for DOC and not detected for T_g and ζ potential.

dried. Separate samples of the original soils were roasted at 375 °C for 16 h with sufficient air to remove the rubbery OC (4, 15).

The two soils and the treated soil samples obtained were characterized in terms of their N₂ surface areas (N₂ SA), glass transition temperatures (T_g), ζ potentials, and DOC contents. All samples were freeze-dried and stored in a desiccator prior to surface analysis and differential scanning calorimetry (DSC) analysis. ζ potential analysis was performed as described previously (16) and DOC contents, extracted with 0.005 mol/L NaCl for 6 h, were determined using a Phoenix 8000 total organic carbon analyzer (Malvern Co., U.K.). The other analyses were conducted as described below. To evaluate the effects of metal cations on the characteristics of the soils, the original soils were extracted with 0.01 mol/L Na⁺, Ca²⁺, or Al³⁺ chloride (soil:solution, 1:100 (w/v)) for 6 h, centrifuged, and freeze-dried and were also used for measurement of the physicochemical characteristics. The results, based on triplicate analyses unless otherwise indicated, are listed in Table 1.

Surface Analysis. Surface area and pore size distribution from 1.7 to 300 nm were determined by applying the Brunauer–Emmett–Teller (BET) equation to multipoint isotherms of N₂ at 77 K with an ASAP-2000 surface area and pore distribution analyzer (Micromeritics Co., USA) as described previously (17, 18).

Differential Scanning Calorimetry Analysis. Glass transition temperature was determined in a TA Instruments Model 2010 differential scanning calorimeter. Samples (~10 mg) were placed in aluminum sample pans, sealed hermetically and subjected to heating from −50 °C and an upper temperature that was approximately 10–30 °C below the thermal degradation temperature (predetermined through thermal gravimetric analysis). A heating rate of 10 °C/min was used, and nitrogen was employed as purge gas. The glass transition temperature is defined as the discontinuity of heat flow (sample specific heat capacity) in a thermal profile between rubbery and glassy states. The T_g was obtained from triplicate separate results since T_g was related to the thermal history of samples, especially of those with low contents of OC, and the T_g of the samples became undetectable at the second heating-cooling cycle (19).

¹H Liquid-State NMR Spectroscopy. The DOC in the soils was subjected to ¹H liquid-state NMR spectroscopy analysis to obtain their chemical group distribution in the presence of metal cations. Briefly, 0.1 g of freeze-dried soil sample and 1 mL of 99.9% D₂O solution containing the corresponding metal cations with a cation concentration of 0.01 mol/L and 100 mg/L NaN₃ were continuously mixed on a shaker for 6 h. Afterward, the mixture was centrifuged for 30 min at 7200g. ¹H NMR spectra of the supernatants were obtained on a Bruker DRX 400 MHz NMR spectrometer under the following experimental conditions. The probe diameter was 5 mm, the recycle delay time was 2 s, the sweep width was 6410 Hz (16 ppm), the line broadening was 0.30 Hz, the scan number was 512, and the detecting temperature was 298 K. The water gate sequence was used to depress the water peak (on water resonance 4.79 ppm) (NB: the water was taken up from the atmosphere during preparation of the samples).

Sorbate. Phenanthrene (98% purity, Aldrich Chemical Co.) in electrolyte solutions (Na⁺, Ca²⁺, or Al³⁺ in chloride) was prepared by diluting phenanthrene stock solution made in high-performance liquid chromatograph (HPLC)-grade methanol. The concentration of methanol in the final solutions was always kept below 0.1% (v/v) to minimize cosolvent effects. No salting out effects was detected at a background concentration of 0.1 mol/L CaCl₂ for phenanthrene solution with a concentration of 1.0 mg/L. The solutions were stored in the dark at 4 °C in amber glass bottles sealed with polytetrafluoroethylene (PTFE)-lined tops.

Sorption Experiments. Samples (0.4000 g) of sorbents were placed into a 45 mL glass centrifuge, and a 40 mL aliquot of phenanthrene solution of varying concentration (0.02–0.8 mg/L) was added. The solid-to-liquid ratios allowed 30–95% of the sorbate to be sorbed at equilibrium. A cation concentration of 0.01 mol/L Na⁺, Ca²⁺, or Al³⁺ and 100 mg/L NaN₃ (pH 6.0) were used respectively as background solutions in sorption experiments in order to evaluate the effects of metal cations on phenanthrene sorption. A CaCl₂ solution of different concentrations (0.01, 0.05, or 0.1 mol/L) and 100 mg/L NaN₃ (pH 6.0) were also used as background solutions to examine the effect of cation concentration on phenanthrene sorption by the soils. The glass centrifuge tubes were tightly sealed with PTFE-lined caps. The tubes filled with sorbent and initial aqueous solution were mixed completely by shaking at 125 rpm in the dark at 20 ± 2 °C for 72 h. The choice of 72 h for equilibration was based on our preliminary sorption rate and equilibrium studies. After centrifugation, phenanthrene in the supernatant solution was determined by HPLC using a reversed-phase 4.6 × 250 mm C₁₈ column (Agilent) with a fluorescence detector for concentrations from approximately 0.5 to 50 µg/L with an excitation wavelength of 230 nm and an emission wavelength of 390 nm, and a diode array detector for concentrations ranging from 50 to 1000 µg/L with a detection wavelength of 254 nm. Isocratic elution was performed at a flow rate of 1.0 mL/min using the mobile phase methanol:water (90:10). The solid-phase sorbate phenanthrene concentration was calculated for each tube from a solute mass balance between the two phases. The sorption experiments and zero sorbent blank assays were all conducted in triplicate. Results of zero sorbent blanks indicated that the loss of phenanthrene other than through sorption by the sorbents was negligible.

Data Analysis. Sorption of PAHs is often described by the Freundlich model ($S = K_f C_e^n$, where S is the amount of sorbate sorbed per unit mass of sorbent (mg/kg) and C_e is the concentration of sorbate in equilibrium solution (mg/L)). The parameter K_f is the Freundlich sorption coefficient [(mg/kg)(L/mg) ^{n}], and n is the isotherm nonlinearity parameter, an indicator of site energy heterogeneity (i.e., the smaller n is, the more heterogeneous the sorption site) (20, 21). To compare different isotherms directly, a modified

FIGURE 1. ^1H NMR liquid-state spectra of DOC from two soils in the presence of metal cations.

Freundlich parameter, K'_f was calculated after normalizing C_e by the supercooled liquid-state solubility (S_s) of phenanthrene (5.902 mg/L) ($S = K'_f C_r^n$, where C_r is the reduced concentration of sorbate; i.e., $C_r = C_e/S_s$) (20, 21). The values of K'_f and n for all sorption isotherms were calculated by the Freundlich equation fitted using Origin 7.0 at the 95% confidence level. Statistical analysis of the results was performed in SPSS for Windows (version 10.0, SPSS Inc.) using ANOVA (Tukey test, $p < 0.05$).

Results and Discussion

Physicochemical Characterization of Sorbents. It is clear from Table 1 that DOC in the two soils decreased significantly in the presence of the polyvalent cations, namely, Ca^{2+} and Al^{3+} ($p < 0.05$). A considerable amount of DOC still remained in the samples even after four consecutive extractions with 0.005 mol/L NaCl in an attempt to deplete DOC, implying that the carbon pools in the soils were actually in a state of homeostasis. With decreasing DOC content, the T_g of the samples tended to increase gradually, and the ζ potential also increased significantly ($p < 0.05$).

Compared with the original soils, N_2 SA increased for the DOC removed samples and decreased significantly ($p < 0.05$) for the samples with polyvalent cations present. However, such changes were not significant ($p > 0.05$) in the samples in the presence of Na^+ (Table 1). The average pore diameter of the samples tended to enlarge with decreasing N_2 SA in the presence of polyvalent cations. Roasting at 375°C changed the soil properties greatly. For instance, the total OC declined from 3.94 and 0.66% to 0.23 and 0.03% in the black soil and red soil, respectively. DOC was totally removed, and the N_2 SA was significantly higher than in the original soils ($p < 0.01$).

^1H liquid-state NMR spectra of DOC from the soils in the presence of metal cations are presented in Figure 1. It should be noted that parts of the DOC components that are bound to mineral surfaces are not completely extracted by the D_2O

FIGURE 2. Effects of metal cations on phenanthrene sorption by two soils (dots) and best fit Freundlich isotherm equation (lines). The values in parentheses represent estimated standard errors of Freundlich parameters.

solvent, and thus the DOC may have been underestimated by the ^1H NMR technique. Apart from a strong signal of water at 4.79 ppm, the two soils showed similar composition in terms of the functional groups of DOC as indicated by the spectra of the Na^+ -extracted DOC samples. Aliphatic carbon was the dominant fraction in the soil extracts. Few, if any, signals from aromatic protons at 8.48 ppm were observed although the soil aromatic moieties would have been protected in hydrophobic regions which were not water accessible. The polyvalent cations significantly decreased the contents of the polar and apolar functional groups from soil solutions as reflected by the signals in the spectra. In the case of the black chernozem soil, the polar groups at 3.61 ppm and aromatic moiety at 8.48 ppm actually disappeared from the soil DOC samples extracted with polyvalent cations. Furthermore, there appeared to be no difference between the effects of Ca^{2+} and Al^{3+} .

Phenanthrene Sorption Isotherms. Phenanthrene sorption isotherms for the two soils in the presence of metal cations are shown in Figure 2, together with the corresponding values of the Freundlich parameters (K'_f and n). The sorption data fit well with the Freundlich models ($r^2 > 0.995$). All the samples exhibited nonlinear sorption for phenanthrene with the values of n below 0.88. A large difference in the phenanthrene sorption capacity was observed between the two soils as reflected by K'_f , as shown in Figure 2, in spite of the presence of cations. Sorption tended to increase gradually with increasing valence of the cations, and the nonlinearity of sorption was also enhanced when Ca^{2+} or Al^{3+} was present compared with the result in the presence of Na^+ ($p < 0.05$).

Enhancement of the capacity and nonlinearity of phenanthrene sorption under increasing concentrations of Ca^{2+} was

FIGURE 3. Effects of cation strength on phenanthrene sorption by soils (dots) and best fit Freundlich isotherm equation (lines). The values in parentheses represent estimated standard errors of Freundlich parameters.

also observed when Ca^{2+} was selected to examine the effect of cation concentration on phenanthrene sorption (Figure 3). The facilitative effect of the cation concentration was significant when 0.05 mol/L was compared with 0.01 mol/L ($p < 0.05$). However, sorption by the soils seemed to be affected less by higher concentrations, i.e., when the cation concentration was at 0.1 mol/L.

Analysis of Mechanisms. Nonlinear sorption of phenanthrene by the soils was observed, which may be viewed as an indicator of the dual reactive domain model (6, 14, 20, 22). The nonlinearity of phenanthrene sorption depends on the rigidity of OC in a given sorbent (2, 10). Among soil OC, the DOC and flexible humic acids are considered to be a soft or rubbery OC while humin is a hard or a relatively condensed phase of OC, which has been confirmed by NMR results (23). It has also been demonstrated that DOC in soil solution is a loosely bound self-association of relatively small molecules, and intermolecular hydrophobic interactions are the predominant binding forces (14, 24). The presence of polyvalent cations caused the flocculation of macromolecules of DOC on soil surfaces through cation bridges between the hydrophilic anionic functional groups of DOC and metal cations (3, 8, 10, 25). Consequently, the content of DOC in solution decreased (Table 1). Our ^1H NMR results confirm that in the presence of polyvalent cations, parts of DOC that once existed in the Na^+ extracts, flocculated and disappeared from the solution (Figure 1) and would be expected to form larger molecules with more rigid structure on the soil surfaces (3, 8). Therefore, part of the DOC that once was soft (or rubbery) carbon tended to become the condensed domains (glassy carbon), and the proportion of glassy carbon in the samples increased accordingly (10). This conclusion was validated by the observed increase in T_g of the soil samples in the presence of polyvalent cations (Table 1).

It was reported that the sorbed DOC resulting from addition of cations was much more reactive and thus had a stronger sorption capacity than the inherent soil OC (26). However, the content of DOC in the two soils was rather low (Table 1), and the enhancement in T_g could not be totally attributed to the flocculation of DOC on soil surfaces and its consequent transition in configuration. Apart from DOC, parts of flexible humic acids on soil surfaces also tend to be condensed and become more rigid on soil surfaces in the presence of polyvalent cations due to the cation bridges between the anionic functional groups of humic acids (8, 10, 25). Therefore the solid rubbery OC fraction on soil surfaces also makes a significant contribution to condensation of OC. In this configuration-modifying process for OC, the trivalent cation (Al^{3+}) is a more effective flocculating agent than the divalent cation (Ca^{2+}), not to mention monovalent cations such as Na^+ (25).

With the hydrophilic groups occupied by the sorbed cations in the inner condensed carbon, more hydrophobic aliphatic groups (for instance, polymethylene) were exposed on the interfacial configuration of the condensed glassy carbon (21). The condensed configuration, substantiated by the DSC and ^1H NMR analysis, could therefore provide more favorable sorption conditions, rendering the reactive hydrophobic areas more accessible for phenanthrene sorption (10, 21). The conversion of rubbery OC from soft to condensed (glassy nature) could therefore account for the higher sorption capacity for phenanthrene and greater degree of nonlinear sorption (2, 6, 10, 26). This is particularly significant ($p < 0.01$) in the case of the black chernozem soil which contained higher contents of both OC and DOC. As for the red soil, although there were lower contents of OC and DOC, significant facilitating effects of metal cations on phenanthrene sorption were still observed ($p < 0.05$). In addition, increased ζ potential indicated the soil surfaces became neutralized by the sorbed cations and thus less hydrophilic, resulting in an enhanced hydrophobic partition of phenanthrene (14, 27).

Although differing in molecular size of N_2 and phenanthrene, the absolute amount of N_2 sorbed by soil or soil components has often been used as an index of "apolar" sorption capacity due to the apolar molecule of N_2 . However, no correlation was observed between K_f' and the N_2 -BET SA of the samples in this study, which is consistent with the results obtained for phenanthrene sorption to black carbon (18, 28) and smectites (17). When the flexible humic acids including DOC became condensed on soil surfaces by polyvalent cations, the condensed carbon would be present in a low-surface area configuration, such as organoclay aggregates (29). In addition, the sorbed DOC would preferentially clog micropores in soil (30). It has been demonstrated that N_2 is unable to reach internal microporosity associated with the condensed humic substances on soil surfaces (18). The condensed OC on soil surfaces, although showing a higher sorption capacity for phenanthrene, provide an artificially external low surface area by the N_2 BET method (2, 18). However, it was still evident that the formation of condensed OC on soil surfaces and the N_2 BET SA were not fit to reflect the sorption capacity of phenanthrene by sorbents (17, 18, 28).

As stated above, the presence of Ca^{2+} cations significantly facilitated the flocculation of DOC and influenced the configuration and structure of the rubbery OC including flocculated DOC on the solid surfaces. As a result, the sorption of phenanthrene to the samples was promoted and the nonlinearity of phenanthrene sorption was strengthened (10, 13, 24). At the low concentration (i.e., 0.01 mol/L CaCl_2), the added Ca^{2+} cations might not result in the complete flocculation of DOC as well as the condensation of other rubbery OC on soil surfaces and a considerable amount of

FIGURE 4. Effects of metal cations on phenanthrene sorption by the DOC-depleted soils (dots) and best fit Freundlich isotherm equation (lines). The values in parentheses represent estimated standard errors of Freundlich parameters.

DOC still existed in the soil solutions. At the high concentrations, DOC gradually disappeared from the soil solution and the rubbery OC was saturated with the cations, and the glassy status of OC would not be further affected by the cations. The facilitation by Ca^{2+} cations of phenanthrene sorption consequently declined, and no significant effects on phenanthrene sorption were obtained between 0.05 and 0.1 mol/L of Ca^{2+} (Figure 3).

To elucidate the role of rubbery OC in the enhanced phenanthrene sorption in the presence of metal cations, the effects of cations on phenanthrene sorption by the samples with DOC removed or roasted at 375 °C were also examined. The sorption capacity of the DOC removed samples (Figure 4) was significantly increased, and the nonlinear sorption of phenanthrene was also enhanced when compared with that of the original soils (Figure 2) in the presence of Na^+ ($p < 0.01$) since DOC could significantly reduce phenanthrene sorption (31, 32). However, the enhancement was gradually attenuated in the presence of the polyvalent cations and became insignificant in the presence of Al^{3+} ($p > 0.05$) for the DOC removed samples compared with the original soils since the effect of DOC involved was weakened by the presence of polyvalent cations. It is noteworthy that facilitating effects of polyvalent cations were also obtained for phenanthrene sorption in the DOC depleted samples (Figure 4). However, the effect was attenuated compared with the original samples, mainly due to the removal of DOC. In the red soil, due to its low OC content, the difference in phenanthrene sorption between the presence of Ca^{2+} and Al^{3+} was not statistically significant ($p > 0.05$) according to the standard error of the measurement. The facilitation of phenanthrene sorption could be ascribed largely to the conversion of the configuration of the flexible humic acids in the samples in the presence of polyvalent cations as stated

FIGURE 5. Effects of metal cations on phenanthrene sorption by soils roasted at 375 °C (dots) and best fit Freundlich isotherm equation (lines).

above. This hypothesis was further confirmed by the results of phenanthrene sorption by the roasted samples. The sorption of phenanthrene was little affected by the metal cations as shown in Figure 5 because almost all the rubbery OC was removed. However, the two roasted samples still showed a distinctive difference in sorption capacity for phenanthrene. Although nonlinearity was attenuated, the nonlinear characteristic was still obvious for the treated black chernozem soil ($n = 0.806, 0.800$, and 0.811 in the presence of Na^+ , Ca^{2+} , and Al^{3+} , respectively). This could be ascribed to the evidence that the soil OC was not totally removed after roasting at 375 °C for 16 h (4, 15). Some of the hard glassy carbon still existed although its structure had been changed. The presence of a limited number of black-carbon-like materials may be responsible for the greater sorption capacity and nonlinear characteristic for phenanthrene (4, 10).

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