

# Constant Asphaltene Molecular and Nanoaggregate Mass in a Gravitationally Segregated Reservoir

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**ABSTRACT:** Spatial gradients in the chemical composition of crude oil are now routinely observed; oils near the top of a reservoir can be enriched in lighter ends, whereas oils near the bottom of a reservoir are typically enriched in asphaltenes. Equations of state capable of modeling these gradients have numerous practical applications, such as predicting variations in fluid properties, the presence of tar mats, and flow connectivity. Because of the great chemical complexity of crude oil, successful modeling of these gradients requires both an understanding of the physical drivers of the gradients and a set of reasonable simplifying assumptions for describing the composition of the crude oil. Gravity is often a dominant force driving fluid gradients, resulting in separation of low-density gas above medium-density oil above high-density water when those isolated phases are present and frequently driving gradients within a phase as well. The impact of gravity in driving gradients depends in part upon the mass and volume of molecules or aggregates in the crude oil. Here, we explore the impact of gravity in segregating asphaltenes of different masses. Asphaltenes were extracted from crude oils from a connected reservoir with a large gradient in asphaltene content and studied with two mass spectrometric techniques: laser desorption laser ionization mass spectrometry (L<sup>2</sup>MS), which measures the mass of asphaltene molecules, and surface-assisted laser desorption/ionization (SALDI) mass spectrometry, which measures the mass of asphaltene nanoaggregates. No significant gradients in the molecule or nanoaggregate mass were observed, suggesting that gravity causes almost no segregation of different molecular or nanoaggregate masses within the asphaltene class. That is, the large concentration gradient of asphaltenes in the reservoir is not accompanied by a large molecular weight gradient within the asphaltene class. These results indicate that asphaltene gradients can be modeled with the simplifying assumption that gravity drives gradients in the concentration of asphaltenes but not the chemical composition of asphaltenes in crude oil.

## ■ INTRODUCTION

It has long been recognized that oil-bearing zones lie beneath gas-bearing zones and above water-bearing zones in connected subsurface reservoirs. These fluid phases are separated by density, because the gravitational potential energy is minimized when fluids are sorted from least dense at the top to most dense at the bottom. In addition, it has been recognized that the composition of reservoir fluids is sorted even within a single phase; crude oil is an extremely complex mixture containing numerous unique molecules, and within the oil phase, certain components (such as asphaltenes) are typically concentrated near the bottom of the column and other components are concentrated near the top.<sup>1–3</sup> Understanding these gradients in fluid composition and their origins is important from not only a fundamental geoscience perspective but also an economic perspective, because these gradients are related to variations in fluid properties,<sup>4,5</sup> flow connectivity of reservoir zones,<sup>6–8</sup> formation of tar mats,<sup>3</sup> fault block migration,<sup>9</sup> and other issues at the reservoir scale.

Many mechanisms can give rise to these gradients.<sup>10–14</sup> Dynamic processes, such as current fluid entry into reservoirs, biodegradation, water washing, and even reservoir migration, can yield disequilibrium fluid gradients.<sup>15</sup> For reservoir fluids that have achieved equilibrium, gravity, entropy, and solubility, all contribute to gradient formation.<sup>2,3,16</sup> For compressible fluids, the hydrostatic head pressure of the oil column yields a

fluid density gradient. This density gradient drives species of low molecular weight to the top of the column and species of high molecular weight to the bottom of the column. In addition, for very large species, such as nanocolloidal asphaltenes, the Archimedes buoyancy forces can be large, yielding gradients of these species.<sup>2,3</sup>

Numerous attempts have been made to model these gradients. The cubic equation of state (EoS) has been the dominant approach to model crude oils, specifically those with dissolved gas. Although the first cubic EoS, the van der Waals equation, was not effective for modeling crude oils, a modified cubic EoS, such as the Peng–Robinson EoS, has been successful.<sup>17</sup> Further modification, such as the Pedersen volume shift correction,<sup>18</sup> makes the cubic EoS effective at modeling gas–liquid properties of crude oils. These developments enable modeling of phase transitions and gradients in the gas/oil ratio in reservoir crude oils. To handle the large number of components in a crude oil, these approaches involve several parameters, such as intermolecular interaction parameters. Extending this gas–liquid model to include a complex mixture of dissolved solids (asphaltenes) involves treating the

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asphaltenes as several different classes, each with its own parameters.

More recently, a different and simplifying approach has been used to model asphaltene gradients. Instead of using equations that trace their roots to the ideal gas law, a polymer solution theory, the Flory–Huggins equation, has been employed. When the gravity term is added to this equation, the Flory–Huggins–Zuo (FHZ) equation is obtained

$$\frac{\phi_a(h_2)}{\phi_a(h_1)} = \exp\left(-\left[\frac{v_a g \Delta\rho(h_2 - h_1)}{RT}\right] + \left[\left(\frac{v_a}{v}\right)_{h_2} - \left(\frac{v_a}{v}\right)_{h_1}\right] - \left[\frac{v_a[(\delta_a - \delta)_{h_2}^2 - (\delta_a - \delta)_{h_1}^2]}{RT}\right]\right)$$

where  $\phi_a(h_i)$  is the asphaltene content at height  $h_i$  in the reservoir,  $v_a$  is the molar volume of the asphaltene particle,  $g$  is Earth's gravitational acceleration,  $\Delta\rho$  is the density contrast between the asphaltene and maltene phases,  $R$  is the ideal gas constant,  $T$  is the temperature,  $v$  is the molar volume of the liquid-phase crude oil, and  $\delta_a$  and  $\delta$  are the solubility parameters of asphaltene and the crude oil.<sup>2,3,19</sup> This model treats petroleum as a two-component mixture (asphaltene and maltene), and it takes into account the molar volume, density, and solubility parameter of each phase. Three forces, gravity, entropy, and solubility, are considered in the model. This model assumes that the properties of the asphaltene phase do not grade continuously in the column, although the maltene solubility parameter (which depends upon the gas/oil ratio) is allowed to vary.

To understand the situations in which each of these models is appropriate, it is necessary to understand the situations in which the assumptions of the models are valid. In particular, each model relies on the simplifying assumption that numerous molecules can be grouped into component classes whose properties are constant or do not vary continuously in an oil column. The asphaltene class alone is highly complex, containing such a large number of unique components as to challenge even the most sophisticated analytical instruments.<sup>20–27</sup> Given this complexity, it is certainly possible that gradients exist within the asphaltene fraction and potentially within other fractions as well. Accurate modeling of the gradient of the asphaltene concentration in crude oil requires understanding if the forces that drive gradients produce simply a higher concentration of asphaltenes in certain locations in the reservoir or different chemical composition of asphaltenes at different locations in the reservoir.

Despite the complexity of asphaltene, some average aspects of their composition have been measured experimentally. Much of the resulting data have been synthesized into the Yen–Mullins model of asphaltenes, which describes hierarchical aggregation of asphaltenes into particles of various sizes, with the dominant size of asphaltene particles in petroleum depending upon the composition of the crude oil.<sup>28,29</sup> According to the model, at low concentration, asphaltenes exist as isolated molecules; at intermediate concentrations, approximately six molecules form a nanoaggregate; and at high concentrations, approximately eight nanoaggregates form a cluster. A similar model based primarily on X-ray and neutron scattering data has been developed.<sup>30</sup> Recent nuclear magnetic resonance (NMR) studies are found to be consistent with this picture.<sup>31–33</sup> The molecule and aggregate sizes described in

these models are used as inputs to the FHZ model of asphaltene content gradients.

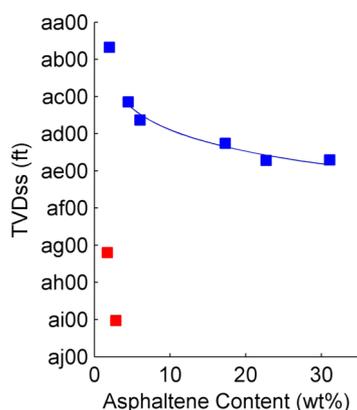
Mass spectrometry is a preferred method to characterize the composition of asphaltenes. All mass spectral analyses begin with volatilizing and ionizing the sample. For analysis of asphaltene molecules, these processes are demanding; they must have a similar efficiency for all components of this complex mixture, must break non-covalent bonds holding asphaltene aggregates together while simultaneously avoiding breaking covalent bonds holding asphaltene molecules together, and ideally must not apply more than one charge to a molecule. Recently, laser desorption laser ionization mass spectrometry (L<sup>2</sup>MS) has emerged as a viable method to meet these specifications.<sup>34–38</sup> In L<sup>2</sup>MS, an infrared (IR) laser pulse desorbs solid asphaltenes from a surface into vacuum and, subsequently, an ultraviolet (UV) laser pulse ionizes the desorbed molecules. Desorption involves rapid, non-specific transfer of energy from the laser to the asphaltene sample.<sup>39</sup> Ionization involves non-resonant absorption of a single photon, which is believed to be a nearly universal method to ionize various molecules with minimal fragmentation.<sup>40</sup> This combination is believed to result in nearly equivalent detection cross-sections for nearly all components of asphaltenes, resulting in accurate measurement of the asphaltene molecular weight distribution.

An alternative method of volatilization and ionization, surface-assisted laser desorption ionization (SALDI), has been shown to volatilize and ionize asphaltenes in the form of nanoaggregates.<sup>41,42</sup> In SALDI, solid asphaltenes are deposited on a surface and struck with a single laser pulse that causes both volatilization and ionization of the asphaltenes. The surface is modified to improve the efficiency of desorption/ionization. This modification facilitates desorption and ionization of asphaltene nanoaggregates at low laser pulse energies (higher pulse energies result in smaller multimers). Volatilization and ionization of asphaltene nanoaggregates permits measurement of the nanoaggregate mass, in this case using a time-of-flight mass analyzer.

Here, L<sup>2</sup>MS and SALDI are used to measure the mass of asphaltene molecules and nanoaggregates from a reservoir with a gravitationally driven gradient in asphaltene content. The magnitude of the gradient is large, exaggerating the impact of gravity in separating different chemical species. It is found that the molecular and nanoaggregate masses of asphaltenes from various locations in this reservoir are nearly identical. This result supports the application of models of asphaltene gradients that incorporate the assumption that asphaltenes can be lumped into a single component whose properties are not continuously graded.<sup>2,3</sup>

## ■ EXPERIMENTAL SECTION

**Asphaltene Samples.** Eight oil samples were taken from a Saudi Arabian anticlinal closure holding a black oil, as described previously.<sup>43–47</sup> Two stacked reservoirs in this structure (referred to as “reservoir A” and “reservoir B”) spanning a depth range of 700 ft were sampled with three wells. The collected oils present a large gradient in asphaltene content, as shown in Figure 1, with the asphaltene content increasing with depth within each reservoir unit. Such gradients are expected for connected reservoirs and predicted by the FHZ EoS.<sup>2,3</sup> Also shown in Figure 1 is a version of the FHZ model of the asphaltene content for reservoir A, with only the gravity term included in the model. Some crude oils (especially those with a high saturate content) with asphaltene contents exceeding 4 wt % are expected to contain asphaltenes in the form of clusters, and fitting the



**Figure 1.** Asphaltene content gradient in reservoirs A (blue) and B (red). The y axis represents depth in the reservoir, expressed as true vertical depth subsea (TVDss). The first digits of the depths have been obscured to preserve reservoir anonymity and are not essential for this analysis, which relies only on relative depths. The measured gradient (points) in reservoir A above 4 wt % asphaltene is well fit by the FHZ EoS, including only the gravity term (line).

measured data above 4 wt % to the model returns an asphaltene particle size of 5.1 nm, demonstrating that, in this reservoir, the asphaltene exists in the form of clusters, as described by the Yen–Mullins model of asphaltene.<sup>28,29,43</sup> Asphaltene was isolated from the crude oils using the standard precipitation procedure with *n*-pentane. Briefly, the oils were mixed 1:40 with *n*-pentane and stirred overnight. The solutions were then vacuum-filtered, and the precipitates were washed with excess *n*-pentane until the rinse ran clear and colorless. The extracted asphaltene was further purified by washing in a Soxhlet extractor for several days.

**L<sup>2</sup>MS.** The L<sup>2</sup>MS technique has been described in detail elsewhere,<sup>41</sup> and this section provides a brief description of the apparatus. A small amount of asphaltene is fixed on a copper platter with double-sided tape and transferred into the vacuum chamber through a vacuum interlock. A pulse of IR light from a CO<sub>2</sub> laser ( $\lambda = 10.6 \mu\text{m}$ ; Alltec GmbH, model AL 882 APS) is focused to a spot ( $\sim 50 \mu\text{m}$  in diameter) on the sample surface using a Cassegrainian microscope objective (Ealing Optics, 15 $\times$ ). Desorbed neutral molecules from the platter surface form a plume in the extraction region of a time-of-flight mass spectrometer (TOF-MS). This plume is then intersected perpendicularly by the vacuum ultraviolet (VUV) output of a pulsed F<sub>2</sub> excimer laser ( $\lambda = 157 \text{ nm}$ ; Coherent, Inc., ExciStar XS 200, Selmsdorf, Germany) and is ionized through single-photon ionization (SPI). The created ions are analyzed in a home-built linear TOF-MS. A dual-microchannel plate (MCP; 20 cm<sup>2</sup> active area; Burle Electro-Optics, Sturbridge, MA) set in a chevron configuration coupled with a large collector anode (Galileo TOF-4000) is used as a detector. Each recorded spectrum is averaged over 100 laser shots.

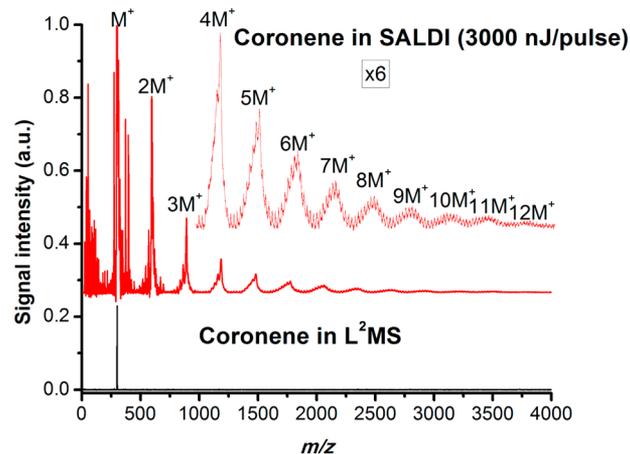
**SALDI.** The SALDI–MS technique has also been described in detail elsewhere.<sup>42</sup> SALDI–MS mass spectra were obtained using a PCS4000 mass spectrometer (Bio-Rad, Fremont, CA). Non-selective normal-phase NP20 arrays (CIPHERGEN, Fremont, CA) were used. The surface of the arrays was modified by silicon oxide groups, which may assist with the desorption/ionization process. A pulsed nitrogen laser with a wavelength of 337 nm was used to desorb and ionize the asphaltene. The laser pulse energy was scanned from 1000 to 6000 nJ/pulse in steps of 250 nJ for each sample, and spectra obtained using conditions maximizing the nanoaggregate signal are presented below. Data were acquired in the positive-ion mode from  $m/z$  0 to 20 000, focused at 4000 Da.

In SALDI–MS experiments, all asphaltene was dissolved in toluene to form solutions with a concentration of 2 mg/mL. These solutions were used to obtain surface concentrations of 96  $\mu\text{g}/\text{cm}^2$  by depositing a drop of 2  $\mu\text{L}$  solution onto a spot (outer diameter of 2.3 mm) on the array. The data analysis was performed using ProteinChip and Ciphergen Express software. The baseline was subtracted with the

following settings: smooth before fitting baseline with 25 points and fit with 100 times expected peak width. Filtering was “on” using an average width of 0.2 times the expected peak width.

## RESULTS AND DISCUSSION

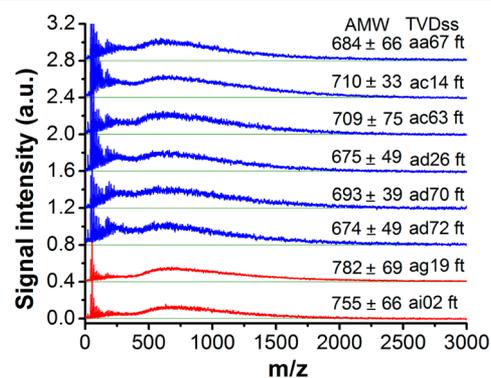
Figure 2 presents mass spectra obtained using L<sup>2</sup>MS and SALDI–MS on a pure compound (coronene) to demonstrate



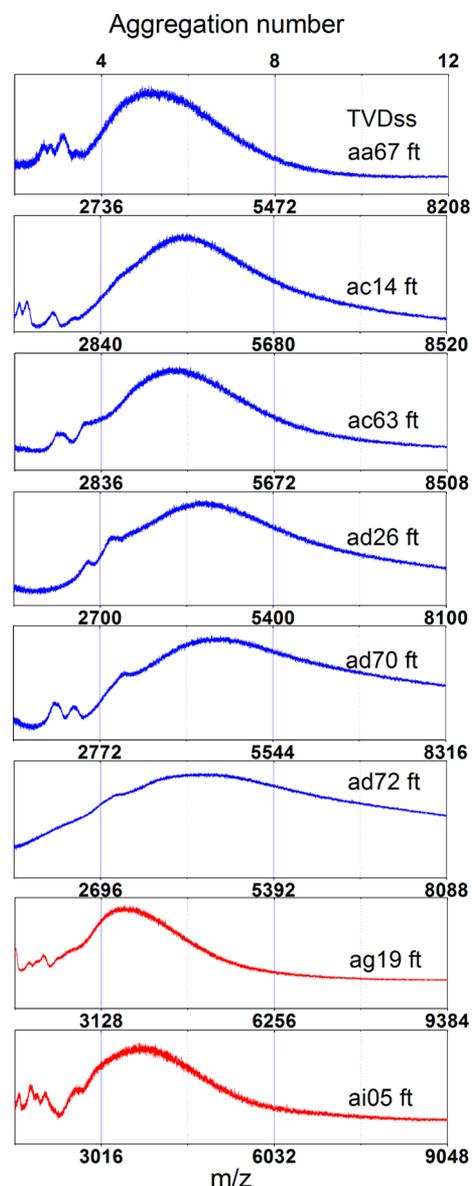
**Figure 2.** Coronene mass spectra from SALDI–MS (upper panel) and L<sup>2</sup>MS (lower panel). The SALDI–MS spectrum contains signals from fragments and multiple aggregates, in addition to the parent ion. In contrast, in L<sup>2</sup>MS, only the parent ion is observed.

the signals obtained with each analysis. In L<sup>2</sup>MS, only the singly charged molecular ion is observed, suggesting that L<sup>2</sup>MS detects components of asphaltene as isolated molecules with little influence from fragmentation, aggregation, and multiple charging, as observed previously.<sup>34,35,38,41</sup> As a result, the L<sup>2</sup>MS signal is considered to be sensitive to molecular weight. In contrast, SALDI promotes aggregation, with aggregates containing up to 12 molecules detectable (Figure 2). Hence, SALDI can be used to measure the mass of aggregated molecules, and for asphaltene samples, SALDI has been shown to be sensitive to the mass of the nanoaggregate.<sup>41,42</sup>

L<sup>2</sup>MS and SALDI mass spectra of the asphaltene from the compositionally graded reservoir are shown in Figures 3 and 4. L<sup>2</sup>MS spectra of the asphaltene samples and their average



**Figure 3.** L<sup>2</sup>MS spectra of the asphaltene. Spectra are arranged in order of depth, with samples from reservoir A (blue) above samples from reservoir B (red). No significant variation in the molecular weights of these samples is observed. Signals at low mass are fragments and are excluded from the average molecular weight (AMW) calculation.<sup>42</sup>



**Figure 4.** SALDI spectra (after background subtraction<sup>42</sup>) of the asphaltenes. Spectra are arranged in order of depth, with samples from reservoir A (blue) above samples from reservoir B (red). No significant variation in the nanoaggregate weights or aggregation numbers of these samples is observed.

molecular weight are presented in Figure 3. Samples are arranged in order of depth, with samples from reservoir A in blue above samples from reservoir B in red. Average molecular weights are near 650 Da, with the signal extending out to 1500 Da. These masses are consistent with the molecular weights determined by L<sup>2</sup>MS for asphaltenes from other reservoirs as well as the molecular sizes determined by time-resolved fluorescence depolarization measurements on other asphaltenes.<sup>34,35,38,48</sup> Most importantly, the results show broad overlap of the molecular mass ranges in all asphaltene samples from these two reservoirs. No indication of heavier asphaltene molecules toward the top or bottom of the reservoir is observed.

SALDI spectra of the asphaltene samples are presented in Figure 4. Samples are again arranged in order of depth. The bottom *x* axis shows the mass-to-charge ratio measured directly

in the SALDI experiment, and the top *x* axis shows the aggregation number (number of molecules per aggregate) determined by dividing the SALDI mass by the molecular mass determined by L<sup>2</sup>MS (Figure 3). The spectra show a maximum near 4000 Da, corresponding to an aggregation number of approximately six molecules per aggregate. These results are consistent with previous SALDI spectra of asphaltenes from other reservoirs and with the assignment of these aggregates as nanoaggregates in the Yen–Mullins model of asphaltenes.<sup>29,42</sup> Additionally, these results are consistent with the size of nanoaggregates of asphaltenes from other reservoirs measured with different techniques, such as NMR,<sup>26,49</sup> direct current (DC) conductivity,<sup>50</sup> and centrifugation.<sup>51,52</sup> The SALDI spectra show broad overlap of all samples studied here, with no indication that asphaltenes from one part of the reservoir form heavier or lighter nanoaggregates than asphaltenes from any other part of the reservoir.

These results show that asphaltenes of different molecular weight or propensity to form nanoaggregates of different weight are not graded in this oil column. The effect of gravity separates components based on density contrast, as shown above. In some cases, there is a correlation between density and molecular weight (for example, methane has the lowest density and lowest molecular weight of any compound typically found in crude oil) such that density gradients can lead to gradients in the average molecular weight of crude oil observed previously.<sup>5</sup> While the range of asphaltene molecular masses is certainly large (see Figure 3), the absence of molecular weight gradients in the asphaltene fraction suggests that there is practically no correlation between the buoyancy of asphaltene particles in the crude oil (in this case, clusters) and the mass of the asphaltene molecules making up the clusters. In particular, the effect of gravity does not appreciably concentrate higher mass asphaltenes toward the bottom of the reservoir, instead concentrating all asphaltenes toward the bottom of the reservoir without leading to a significant variation in the asphaltene molecular weight throughout the reservoir.

## CONCLUSION

The composition of crude oil is typically graded, varying from location to location even in connected and equilibrated reservoirs. Several factors drive the formation of fluid compositional gradients, and in many cases, gravity is one of the strongest drivers. Crude oil is a complex mixture containing components of a wide range of molecular weights, which partially determines the magnitude of gravitational segregation in reservoir fluids. Spatial gradients in the average molecular weight of crude oil within a reservoir have been observed.<sup>5</sup> The asphaltene fraction of crude oil is itself a complex mixture containing components of a wide range of molecular weights. Here, we find that gravitational segregation does not separate asphaltenes of different molecular weight. Even in this reservoir, which presents a large gradient in the concentration of asphaltenes (order of magnitude) driven primarily by gravity, the molecular weight and nanoaggregate weight of asphaltenes show almost no variation throughout the reservoir. In combination with a consistent sulfur chemistry of the asphaltenes from this reservoir,<sup>47</sup> this result that the asphaltenes also have a consistent molecular weight and form nanoaggregates of a consistent weight suggests that gravitational segregation results in gradients in the concentration of asphaltenes in crude oil but not in the chemical composition of those asphaltenes.

These results have implications regarding modeling of gradients in oil composition. The FHZ EoS can successfully model asphaltene content gradients, even in a reservoir in which the magnitude of the gradient is large. The FHZ EoS and the underlying Yen–Mullins model rely on the simplifying assumption that the chemical composition of asphaltenes is ungraded, even while the concentration of asphaltenes in the crude oil is graded. That assumption is consistent with these results, suggesting that the FHZ EoS is properly constructed to model such gradients. The cubic Peng–Robinson EoS can also model this asphaltene content gradient, but that model requires either the assumption of a large asphaltene molecular weight (60 000 Da) or varying asphaltene molecular parameters.<sup>53</sup> Those assumptions are inconsistent with the low and ungraded asphaltene molecular weights measured here, suggesting that the cubic Peng–Robinson EoS is not suitable for modeling these asphaltene gradients.

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### Notes

The authors declare no competing financial interest.

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