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Bacteria as Cloud Condensation Nuclei (CCN) in the Atmosphere

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Abstract: Bacteria activation and cloud condensation nuclei (CCN) formation have been studied in the atmosphere using the classical theory of heterogeneous nucleation. Simulations were performed for the binary system of sulfuric acid/water using laboratory-determined contact angles. Realistic model simulations were performed at different atmospheric heights for a set of 140 different bacteria. Model simulations showed that bacteria activation is a potentially favorable process in the atmosphere which may be enhanced at lower temperatures. CCN formation from bacteria nuclei is dependent on ambient atmospheric conditions (temperature, relative humidity), bacteria size, and sulfuric acid concentration. Furthermore, a critical parameter for the determination of bacteria activation is the value of the intermolecular potential between the bacteria's surface and the critical cluster formed at their surface. In the classical nucleation theory, this is parameterized with the contact angle between substrate and critical cluster. Therefore, the dataset of laboratory values for the contact angle of water on different bacteria substrates needs to be enriched for realistic simulations of bacteria activation in the atmosphere.

Keywords: bacteria activation; CCN formation; heterogeneous nucleation; binary nucleation

1. Introduction

Primary biological aerosol particles (PBAPs) comprise an important source of natural origin particles in the atmosphere and incorporate a large variety of microorganisms such as bacteria and viruses, as well as particles produced from abrasive processes [1,2]. Transmission of microorganisms to the air may have significant impacts on public health, and therefore characterization of bioaerosols has been performed at different working environments (e.g., [3,4]).

Furthermore, airborne microorganisms have been studied in the scientific literature as potential candidates for cloud condensation nuclei (CCN) and ice nuclei (IN) in the atmosphere [2,5,6]. In particular, bacteria provide effective surfaces to act as CCN and IN [6–9]. Franc and DeMott [9] found that specific strains of the pathogenic bacteria *Erwinia carotovora* that are emitted from plants were activated at supersaturations larger than 1%. Surface coating on bacteria and other microorganisms was also studied to determine the changes on their nucleation properties [10,11].

Typical sizes for bacteria are between 0.5 and 5 microns in diameter, whereas bacteria agglomerates can reach diameters ranging from 3 to 8 microns. Size distribution characteristics of airborne microbes have been presented by Zhai et al. [12]. Hygroscopic growth of bacteria that are generally hydrophobic can be determined from the contact angle of water on the surface of particles. The value of the contact angle determines the wettability of surfaces, and values as low as 20° were reported in the literature, which indicates their ability to act as CCN in the atmosphere [13]. Laboratory data have shown that ice nuclei without any coating have contact angles below 20° for *Pseudomonas syringae* bacteria, whereas for mineral particles coated with sulfuric acid the contact angle reaches 60° [10]. This is in agreement with previous studies that show that *P. syringae* has a good nucleation potential for IN [14,15]. The theory of

heterogeneous nucleation can be used for the study of CCN formation of bacteria [16–18], including the measured contact angles. A numerical study of contact angle parameterizations for immersion freezing was performed by Ickes et al. [19] using the classical nucleation theory. Similar parameterizations for different minerals were adopted for use in general circulation models (GCMs).

Bauer et al. [6] showed also that a set of both gram-positive and -negative bacteria was activated at supersaturations between 0.07% and 0.11%, which also highlights their ability to act as CCN in the atmosphere. Changes in CCN concentration may affect cloud structure and dynamics, which may further influence the aerosol–cloud radiative forcing and the climate [20]. An important influence on CCN formation may arise from the aging of airborne bacteria and their shape. The shape may affect the contact angle, while the aging process involves changes in the cell wall and extracellular materials that could affect the cluster formation [10,11].

Concentrations of bacteria at the range of 10^4 particles/m^3 were measured in the atmosphere [1] with average number fluxes equal to 10^2 particles/(m^{2}s) [7]. However, no significant effect was found on the influence of biological origin aerosol particles on cloud formation, mainly due to their low atmospheric concentrations [21]. However, the quantification of the emission sources of microorganisms from different surfaces is far from complete, which implies a possible underestimation of the effects of microorganisms on the climate [22]. These results were supported by recent findings on the influence of a fungus genus *Fusarium* which can be important for ice nucleation and cloud formation [23]. Furthermore, several studies revealed the need to better characterize the ambient concentrations and biodiversity of biological particles in the atmosphere [1].

In the current study, the theory of binary nucleation of the sulfuric acid/water system was used to determine the conditions under which the activation of bacteria (CCN formation) occurs at tropospheric conditions. The mechanism of surface diffusion was incorporated in the calculations of particle activation using a previously developed kinetic approach for nucleation [18,24].

2. Kinetic Model of Heterogeneous Nucleation

The activation of bacteria in atmospheric conditions can be described using the classical theory of heterogeneous nucleation, which occurs at lower saturation ratios than homogeneous nucleation. The surface of bacteria is considered wettable by water and at the same time water insoluble. The heterogeneous nucleation theory on insoluble particles for binary systems from the vapor-to-liquid phase [17,25] has been adopted in the current study to evaluate the activation of airborne bacteria. The scientific literature has recognized the importance of sulfuric acid on the activation of pre-existing insoluble particles [20] and therefore we studied the sulfuric acid/water system for particle activation and CCN formation. Specifically, sulfuric acid has been used in CCN studies due to the interaction of the molecules through the hydrogen bonds, which is important in the formation of the small atmospheric clusters.

The classical heterogeneous nucleation theory is a phenomenological theory, which examines the nucleating droplet as a group of molecules that interact strongly among themselves and weakly with the rest of the system. According to the classical theory, the nucleating cluster is treated with equilibrium thermodynamics as a macroscopic droplet whose free energy of formation depends crucially on the bulk surface tension. The nucleation rate depends exponentially on the reversible work of cluster formation since nucleation is an activated process. The theory relies on a macroscopic description of an embryo in contact with a substrate using the concept of the contact angle θ [17,25]. The interaction between the liquid embryo and the solid substrate has been described in the classical model with the help of Young's equation, $\cos\theta = m = \frac{\gamma_{vs}-\gamma_{ls}}{\gamma_{lv}}$, where θ is the contact angle between the substrate and the liquid embryo. The critical droplet composition is given by the composition at the saddle point [18].

In the classical theory, the free energy of formation of the critical cluster on a curved surface can be expressed as follows [25]:

$$\Delta G^*_{\text{het}} = \Delta G^*_{\text{hom}} f(\cos\vartheta), \quad (1)$$

where the angle ϑ, which can vary from 0 to 180°, is the contact angle between the nucleus and the solid substrate. For water nucleation, the solid is considered hydrophobic or hydrophilic according to whether the contact angle is greater or less than 90°.

The critical value for the Gibbs free energy in the homogeneous case is obtained from the following expression [17]:

$$\Delta G^*_{hom} = \frac{2}{3}\,\pi\, r^{2*}\,\gamma_{sl}\, f(m,x), \tag{2}$$

where $f(m, x)$ is a function of the cosine of the contact angle and $x = \frac{R_p}{r^*}$ (R_p denotes the radius of the pre-existing aerosol particle and r^* is the radius of the critical nucleating cluster).

The heterogeneous nucleation rate J_{het} can be expressed as a product of a kinetic prefactor J^o_{het} multiplied by an Arrhenius factor:

$$J_{het} = J^o_{het}\ \exp\left(-\frac{\Delta G^*_{het}}{k_B T}\right), \tag{3}$$

where k_B is the Boltzmann constant.

The kinetic prefactor can be expressed as follows:

$$J^o_{het} = R_{growth}\, N\, Z, \tag{4}$$

where R_{growth} is the cluster growth rate, Z the Zeldovich non-equilibrium factor, and N is the product of the total number of molecules adsorbed per unit of seed particle surface area (N_{ads}) and the available surface area (A_{ads}) for adsorption per seed particle [25].

A detailed description of the theory of heterogeneous nucleation can be obtained from [18,25–27]. The mechanism of surface diffusion has also been included in the nucleation process, leading to higher nucleation rates [16,18,27,28]. The kinetic model was validated against water nucleation on planar substrates [18]. In the atmosphere, it is important to know the activation probability $P_d(t)$ for heterogeneous nucleation to occur, which corresponds to the ratio of the activated particles $N_d(t)$ to their initial concentration $N_{d,in}$ [26]:

$$P_d(t) = \frac{N_d(t)}{N_{d,in}} = 1 - \exp(-kt) = 1\ - \exp\left(-\int_0^{\tau \mathrm{int}} J\ dt\right), \tag{5}$$

where t is the time, τ_{int} is the time interval under consideration, and k is the activation rate per pre-existing particle.

3. Results and Discussion

Atmospheric simulations of bacteria activation were performed using a model of heterogeneous nucleation for the binary system of sulfuric acid/water [18,24]. Vertical profiles of temperature and gaseous sulfuric acid and water concentrations were obtained from Hamill et al. [29] (see Table 1). In the calculations, the mechanism of surface diffusion was also incorporated using a typical value of the diffusion coefficient (10^{-8} m^2/s).

Previous ice nucleation studies have shown a typical average contact angle of 20° for *P. syringae* bacteria, which is a common ice nucleus [10]. Therefore, these bacteria have the potential to be activated as well in the lower troposphere. Activation of *P. syringae* bacteria (mean bacteria radius, r_p = 0.3 μm) was studied at surface level conditions ([H_2SO_4] = 3.58 × 10^8 molecules/cm^3; [H_2O] = 7.1 × 10^{16} molecules/cm^3) [29] for two different ambient temperatures (T = 298 K and T = 273 K), as shown in Figure 1. The activation of *P. syringae* is favorable at low contact angles for both temperatures, and at the lower temperature (T = 273 K) the activation occurs at contact angles close to 90°. At 298 K ambient temperature, the activation occurs for contact angles lower than 50°. In both

cases the simulations revealed the high activation potential of *P. syringae* bacteria, which indicate nucleation probability of one at contact angles of 20 in the troposphere. This is in agreement with experimental studies on the high ice nucleation potential of *P. syringae* [10].

Table 1. Temperature (K) of gaseous sulfuric acid ($[H_2SO_4]$) and water ($[H_2O]$) concentrations (molecules/cm^3) vs. altitude used for the nucleation calculations in the atmosphere (values adopted from Hamill et al. (1982)).

Altitude (km)	Temperature (K)	$[H_2SO_4]$ (Molecules/cm^3)	$[H_2O]$ (Molecules/cm^3)
0	288	3.58×10^8	7.1×10^{16}
2	275	2.03×10^8	3.6×10^{16}
4	262	9.29×10^8	1.3×10^{16}
6	249	3.85×10^7	4.6×10^{15}
8	236	1.73×10^7	1.3×10^{15}
10	223	8.83×10^6	2.2×10^{14}
12	219	5.50×10^6	4.3×10^{13}
14	216	1.01×10^6	9.3×10^{12}
16	216	1.12×10^5	7.0×10^{12}
18	216	3.67×10^4	5.2×10^{12}
20	217	4.20×10^4	4.0×10^{12}
22	219	8.68×10^4	2.9×10^{12}
24	221	1.93×10^5	2.1×10^{12}
26	223	4.59×10^5	1.5×10^{12}
28	225	1.23×10^6	1.2×10^{12}
30	227	2.88×10^6	9.8×10^{12}

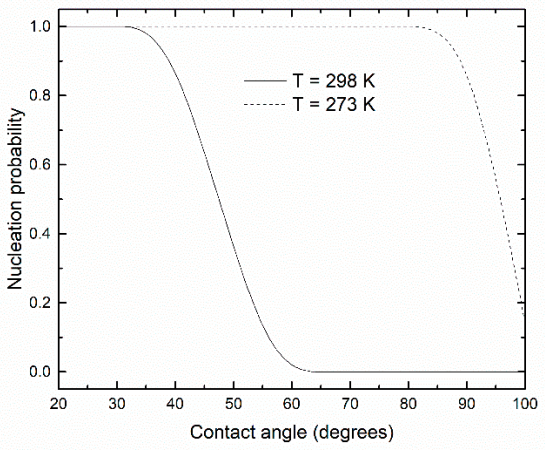

Figure 1. Nucleation probability of the sulfuric acid/water system versus the contact angle of *Pseudomonas syringae* bacteria (r_p = 0.3 μm) at surface level at ambient temperatures of 298 K and 273 K.

Figure 2 shows the heterogeneous nucleation rate (embryos/(m^2 s)) for two bacteria, *P. syringae* and *P. aeruginosa* (mean bacteria radius, r_p = 0.3 μm) in the atmosphere at different altitudes. Vertical profiles for temperature and gaseous concentrations of water and sulfuric acid were obtained from Hamill et al. (1982). Contact angles of 20 and 106° were adopted for *P. syringae* and *P. aeruginosa*, respectively, as determined from experimental studies [10,13]. Bacteria with different contact angles have very different behavior in their activation characteristics, and *P. aeruginosa* is known to have a low probability of activation at altitudes of 4–15 km. At altitudes of 0–4 km, the *P. aeruginosa* does not have the ability to be activated since the nucleation rate is low.

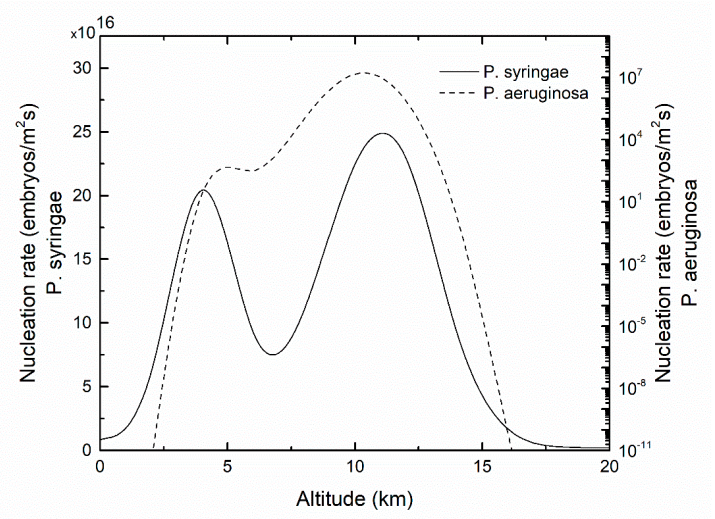

Figure 2. Heterogeneous nucleation rate (embryos/(m^2 s)) versus altitude for *P. syringae* and *P. aeruginosa* bacteria (r_p = 0.3 μm).

Simulations were also performed for *Actinomyces naeslundii 5519* (mean bacteria radius, r_p = 1 μm; θ = 62) at surface level at different ambient temperatures [13], as shown in Figure 3. Activation was observed for temperatures lower than 295 K, which supports previous field observations for the activation of atmospheric microorganisms at the upper troposphere [2]. A critical parameter which determines the activation of bacteria is the value of the contact angle that determines the intermolecular potential between the activating embryo and the bacteria substrate. Therefore, reliable measurements [13] for the contact angle between water and different bacteria substrates are crucial in the current simulations.

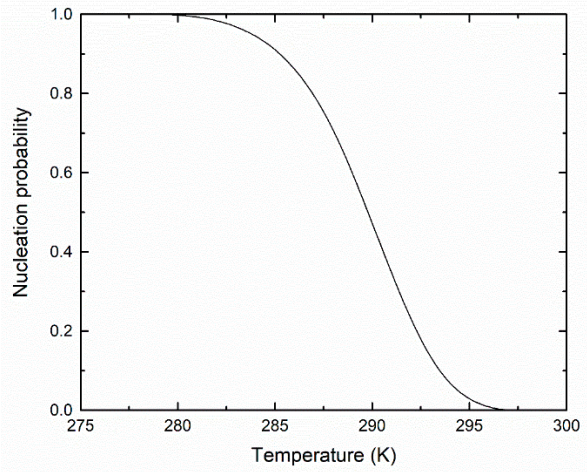

Figure 3. Activation of *Actinomyces naeslundii 5519* (mean bacteria radius, r_p = 1 μm; θ = 62°) versus temperature at surface level for the sulfuric acid/water system. Sharma and Rao [13] determined the contact angle of 140 bacterial cell surfaces with water, and contact angles ranged from 16 to 106°. The specific number of bacteria and yeast strains were chosen since they comprise a reference guide to microbial cell surface hydrophobicity based on contact angles. The isolates were obtained from American Type Culture Collection (ATCC) and National Collection of Type Cultures (NCTC) strains and other standard strains in hydrophobicity research [13].

Figure 4a shows the relative frequency (%) (probability density function) of the different bacteria cells versus the contact angle which ranges from hydrophilic to hydrophobic. Higher frequency of hydrophilic bacteria was encountered in the measurements, which indicates easier activation of

these bacteria cells in atmospheric conditions. Figure 4b presents the nucleation probability versus temperature for a distribution of bacteria cells, as measured by Sharma and Rao [13] (mean bacteria radius, r_p = 1 μm) at surface level [29]. With decreasing ambient temperature, the probability of activation of bacteria increases due to the lower energy requirement for the formation of critical clusters. Therefore, activation of bioaerosols to CCN occurs more effectively at lower ambient temperatures. At lower temperatures, the critical nuclei contain a smaller number of molecules due to the difference between the gaseous and liquid activities of sulfuric acid and water [18].

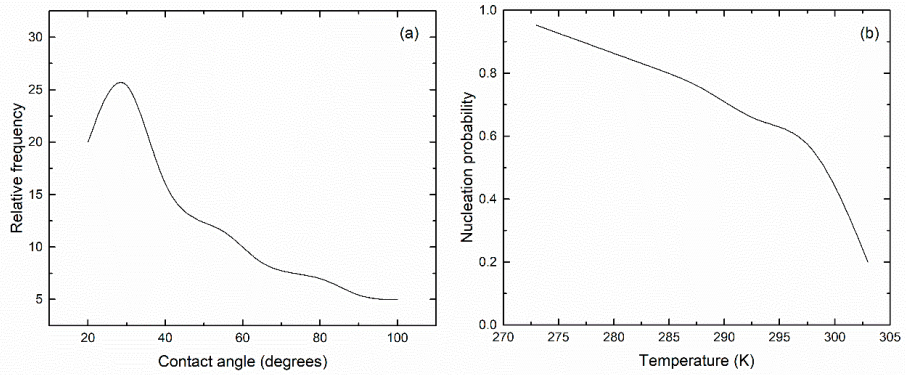

Figure 4. (**a**) Relative frequency (%) of contact angle occurrence at 140 bacterial cell surfaces with water (Sharma and Rao [13]). (**b**) Nucleation probability of the distribution of the 140 bacterial cells versus temperature (mean bacteria radius, r_p = 1 μm) at surface level of the sulfuric acid/water system.

Realistic simulations were performed for CCN formation in the atmosphere using the distribution of bacteria determined by Sharma and Rao [13] and a time interval for activation of 1 h, as shown in Figure 5. The probability is higher at higher altitudes, with probability close to 0.5 at surface level. In the calculations, we adopted mean values of temperature and gaseous concentrations at different altitudes. In addition, a mean bacteria size of 1 μm was used in the calculations. In real atmospheric conditions, there is strong variability of the parameters which determine the nucleation rate and activation of particles, and therefore fluctuations of CCN production are expected to occur. These results are in agreement with field observations for the activation of bacteria in the atmosphere (e.g., [6]).

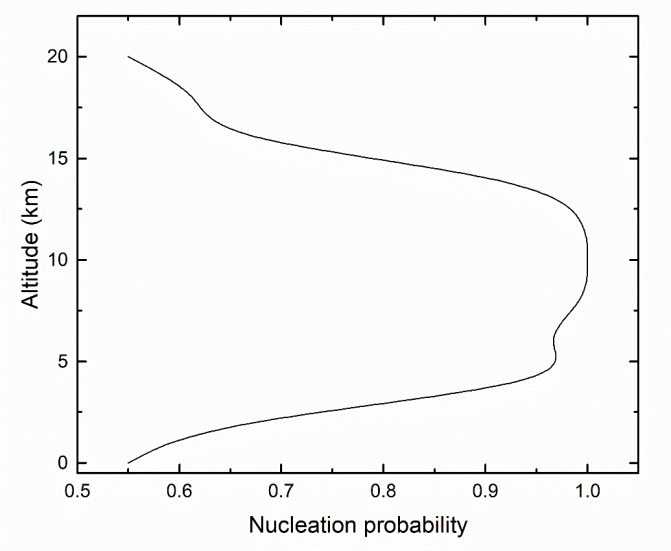

Figure 5. Nucleation probability of the distribution of the 140 bacterial cells (Sharma and Rao [13]) at different altitudes of the sulfuric acid/water system.

The influence of particle size on the CCN production is shown in Figure 6 at two different ambient temperatures (T = 292 K and T = 293 K). The simulations were performed at surface altitude (θ = 55°) and they reveal the strong influence of particle size and ambient temperature on bacteria activation. Increasing the particle size results in easier particle activation due to the increased surface area [18,30]. In the atmosphere, bacteria can be attached to other airborne particles or can be found as agglomerates of different bacterial cells, and consequently the mean aerodynamic diameter was observed in sizes between 2 and 4 μm, whereas single bacteria have diameters closer to 1 μm [1]. Therefore, the bacterial activation in the atmosphere is a more complex phenomenon, and the inclusion of active sites may incorporate the activation of non-homogeneous surfaces [26].

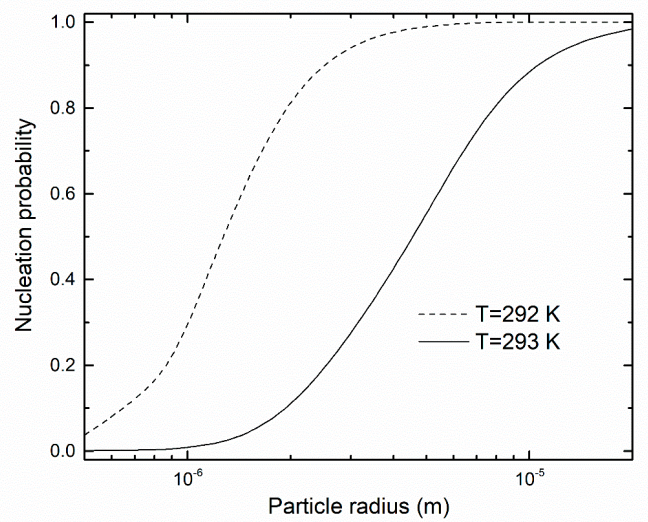

Figure 6. Nucleation probability versus particle radius at two different ambient temperatures (T = 292 K and T = 293 K) at surface level (contact angle θ = 55°).

4. Conclusions

A model for heterogeneous nucleation incorporating the process of surface diffusion was used for the simulation of bacteria activation in the atmosphere. The simulations performed for the activation of bacteria incorporated the classical theory of binary heterogeneous nucleation (water/sulfuric acid) using experimentally determined values for the contact angle. Model simulations revealed that bacteria activation and further CCN formation is a favorable process in the atmosphere, with higher probability at lower temperatures. Activation of bacteria was found to be more favorable at the upper troposphere, and specific bacteria including *P. syringae* have a better nucleation probability and are potential CCN nuclei.

A model of the classical theory of heterogeneous nucleation can be also integrated in GCMs for evaluating the effectiveness of bacteria to act as CCN. However, reliable bacteria distribution data are needed, in combination with available laboratory measurements of contact angle values for realistic simulations of bacteria activation in the atmosphere. However, the incorporation of sulfuric acid may lead to changes in the contact angle measurements. As previously described in [18], there were experimental studies [31] for the *n*-propanol/water vapor binary mixture, and in respect to Ag substrates the theory of heterogeneous nucleation showed a major disagreement with the available data, perhaps due to the differences between macroscopic and microscopic contact angles. The estimation of contact angles for binary systems can be performed using heterogeneous nucleation experimental data, such as experimental data for the binary heterogeneous nucleation of *n*-nonane and *n*-propanol systems. A fast expansion chamber was used in this study and the determination of particle number concentration and particle growth was performed using constant-angle Mie scattering. The observed nucleation probabilities can be fitted using the classical theory of heterogeneous nucleation, and determining

implicitly the value of the contact angle. Therefore, detailed experimental laboratory studies are necessary for the sulfuric acid/water system in order to determine the contact angle values.

Perturbations of atmospheric characteristics such as temperature, relative humidity, and sulfuric acid concentration may result in variability of bacteria activation. Particle size also influences the nucleation rate, and consequently the nucleation probability, with larger particles becoming more easily activated. Even though those bacteria are potential candidates for CCN formation as shown in the current simulations, their effectiveness in cloud formation and further climate implications have to be studied with respect to their atmospheric abundance and emission characteristics. Understanding the influence of bioaerosols in cloud dynamics and climate remains one of the most challenging topics in atmospheric science.

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