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## First gaseous ion composition measurements in the exhaust plume of a jet aircraft in flight: Implications for gaseous sulfuric acid, aerosols, and chemiions

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**Abstract.** Mass spectrometric composition measurements of gaseous negative ions have been made in the exhaust plume of a commercial jet aircraft (Airbus A310) in flight at altitudes around 10.4 km and at two plume ages around 3.0 and 3.6 s. Negative ions observed inside the exhaust plume are mostly  $\text{NO}_3(\text{HNO}_3)_m$  and  $\text{HSO}_4(\text{HNO}_3)_m$  with  $m \leq 2$ . Outside the plume in the "background" atmosphere the same negative ion species with the same  $R = (\text{HSO}_4(\text{HNO}_3)_m)/(\text{NO}_3(\text{HNO}_3)_m)$  were observed. This indicates that the ions observed in the plume were entrained ambient atmospheric ions. By contrast no indications for negative chemiions (with masses  $\leq 1100$  amu) produced by the Airbus engines were found in the plume. Furthermore our measurements indicate a modest decrease of the total concentration of entrained negative ions in the plume compared to the ambient atmosphere outside the plume. This decrease may be due to ion-removal by ion-attachment to aerosol-particles and/or ion-recombination with positive chemiions. We propose that the observed entrained ions can serve as probes for important plume components including gaseous sulfuric acid, aerosol particles and chemiions. Making use of this analytical potential we infer upper limits for the gaseous sulfuric acid concentration, total aerosol surface area density, and positive chemiion concentration. We conclude that initially formed gaseous sulfuric acid must have experienced rapid gas-to-particle conversion already in the very early plume at plume ages  $< 1.6$  s.

### Introduction

Jet engines produce chemiions and sulfur trioxide ( $\text{SO}_3$ ) which may have important roles in the formation of aerosol particles and eventually even water contrails. Sulfur trioxide undergoes rapid conversion to gaseous sulfuric acid already in the very early exhaust plume [cf. *Reiner and Arnold*, 1993, *Lovejoy et al.*, 1996, *Jayne et al.* 1997]. Together with water vapor gaseous sulfuric acid may undergo bi-molecular nucleation and condensation leading to condensed sulfuric acid/water mixtures [cf. 1995, *Zhao and Turco*, 1995]. Nucleation may proceed via a homogeneous mechanism leading to new aerosols or via a heterogeneous

mechanism (on soot particles) leading to at least partial sulfuric acid/water-coating of soot. Such coating may be necessary to activate initially hydrophobic soot-particles to become hydrophilic and thereby to become nuclei in water vapor condensation leading to water contrails.

Chemiions may have an important role in promoting homogeneous nucleation [*Frenzel and Arnold*, 1994; *Yu and Turco*, 1997, 1998] as well as aerosol growth via coagulation. The first chemiion composition measurements in jet fuel combustion in the laboratory revealed that negative chemiions are mostly of the type  $\text{HSO}_4(\text{H}_2\text{SO}_4)_m(\text{H}_2\text{O})_n$  [*Frenzel and Arnold*, 1994]. These ions are formed by ion-molecule reactions involving precursor chemiions and gaseous sulfuric acid as was concluded by these authors. The ion-molecule reactions in question are:



followed by replacement of  $\text{HNO}_3$ -ligands by  $\text{H}_2\text{SO}_4$ . These reactions have originally been proposed by *Arnold and Fabian* [1980] and subsequently measured in the laboratory. It was found that reactions (1) occur close to collision rate with rate coefficients of about  $2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  [*Viggiano et al.*, 1997]. Recently the first composition measurements of negative chemiions have been made in the exhaust plumes of jet engines at the ground [*Arnold et al.*, 1998]. Again the major ions were found to be of the type  $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_m$ .

The MPIK-Heidelberg group has repeatedly exploited their ion composition measurements to infer gaseous sulfuric acid-concentrations and termed this indirect analytical method PACIMS (Passive Chemical Ionization Mass Spectrometry). PACIMS measurements of gaseous sulfuric acid in jet engine exhaust at the ground indicate an efficiency  $\epsilon$  for fuel-sulfur conversion to gaseous  $\text{H}_2\text{SO}_4$  of 1-2% [*Arnold et al.*, 1997, 1998].

The exhaust plume of a jet aircraft in flight cannot be probed by an ion mass spectrometer at the same small plume ages  $t_p$  as is possible at the ground ( $t_p$  as small as 10 ms but more typical 100 ms). In flight smallest plume ages which can be probed are more like 0.5 s for a wide body aircraft. At such plume ages chemiion-concentrations are expected to be much smaller compared to smaller  $t_p$  accessible at the ground. This is due to plume dilution, ion-ion recombination, and possibly also chemiion-attachment to aerosol particles. Furthermore as described by *Yu and Turco* [1997, 1998] by  $t_p = 0.5$  s chemiions may also have grown quite substantially due to ion-clustering of gas-molecules particularly  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$ .

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Besides chemiions the plume should contain also entrained ambient atmospheric ions which can serve as probes for gaseous sulfuric acid, aerosols and in addition also for chemiions. Entrained ions may react with gaseous sulfuric acid and thereby change their chemical nature. Entrained ions may also become removed by attachment to aerosols and by recombination with oppositely charged chemiions. Note that gaseous sulfuric acid, aerosols and ions in the plume are much more abundant than gaseous sulfuric acid, aerosols and ions outside the plume.

The present paper reports on the first mass spectrometric measurements of gaseous negative ions in the exhaust plume of a jet aircraft in flight.

## Experimental

We have used an aircraft-based ion mass spectrometer (IOMAS) of MPI-K for measurements of the total concentration and composition of gaseous negative ions. IOMAS which was developed, built, and operated by MPIK-Heidelberg has a mass range of 1100 amu (atomic mass units). For details of the IOMAS-instrument see *Krieger and Arnold [1994]*. The measurements to be reported here took place at an altitude of 10.4 km in the young exhaust plume of a Lufthansa Airbus (A310, engine-type: CF6-80C2A2) when IOMAS flew onboard the DLR-research aircraft "Falcon" at distances of 400 m to 800 m behind the Airbus corresponding to plume ages  $t_p$  of 2.0 to 4.5 s. The ambient atmospheric background temperature and relative humidity were 215 K and 15 %, respectively. A short visible water contrail was present during the plume penetrations.

Our ion-composition measurements are affected by several problems including: (a) Electric field-induced collisional dissociation of cluster ions during sampling by an "orifice-probe"; (b) sampling-line losses of ions which depend somewhat on ion-mass; (c) a limited mass range of 1 - 1100 atomic mass units.

Importantly the conclusions of the present paper are not significantly affected by the above problems (a), (b), and (c) since they rely only on the measured abundance ratio  $R$  of ions with  $\text{NO}_3^-$  and  $\text{HSO}_4^-$  "core ions" (see above) and relative changes of the total ion-concentration.  $R$  is not changed by (a), and  $R$  is not substantially changed by (b) since the members of the above two ion-families have similar masses. The limited mass range of IOMAS (c) may not allow to detect chemiions if these grew very large.

The statistical uncertainty of our ion measurements at cruise altitude is limited by the effective residence time of the research aircraft within the exhaust plume. Therefore for each plume penetration phase data of several individual plume encounters have been added. Thus the present ion-based measurements of gaseous sulfuric acid, total aerosol surface area density, and total positive chemiion concentration only yield mean values over the cross section of the plume.

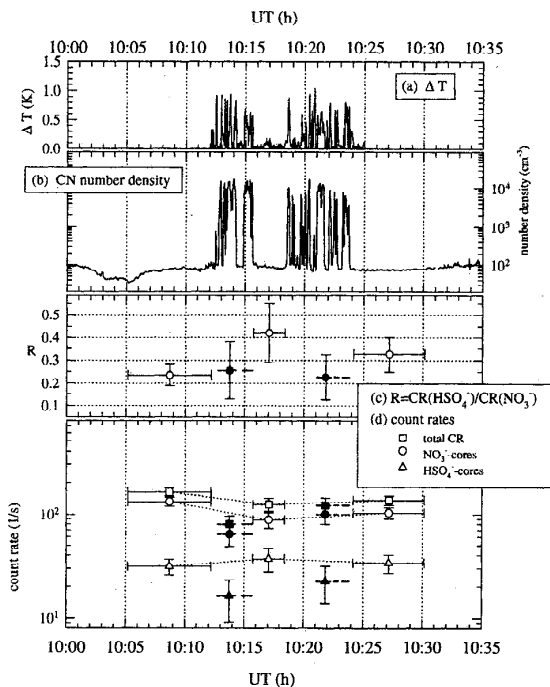
Importantly, gaseous sulfuric acid-detection by PACIMS is not affected by wall losses of gaseous sulfuric acid in the flowtube since the relevant ion-molecule reactions take place outside the flowtube of the instrument. Absolute total ion concentrations in the plume can be obtained by "calibrating" IOMAS in the background atmosphere outside the plume using ambient ions whose concentration is well known. The estimated uncertainty of the measured ion abundance ratio  $R$  is  $\pm 50\%$  if ions with mass numbers  $> 1100$  do not significantly contribute. The estimated uncertainty of relative changes of total ion concentrations (inside compared to outside the plume) is  $\pm 30\%$ .

As a sensitive probe for plume penetration a condensation nucleus counter (type: TSI CPC 3010) of MPI-K Heidelberg was integrated into the sampling tube of the IOMAS-instrument. The counter measured CN with radii equal to or larger than 10 nm which are expected to be mainly soot particles. Peak values of the measured CN number density indicate plume penetrations, but are only lower limits of the absolute number density of CN inside the plume due to coincidence counting.

## Results and Discussion

Figure 1 shows the time-plots of  $\Delta T$  (plume-temperature minus ambient temperature; panel a) and CN-concentrations (panel b). Plume-penetrations which are marked by elevated  $\Delta T$  and CN-concentrations occurred mainly during two time-intervals namely 10.12.30 - 10.15.45 UTC (Phase 1) and 10.21.00 - 10.24.00 UTC (Phase 2). Individual plume penetrations mostly did not last longer than 60 s. During phase 2 individual plume penetrations are mostly shorter compared to phase 1. This may be accompanied by less perfect plume penetrations with more plume-edge sampling (see below). Mean plume ages (age of the plume parcel probed) were 3.6 s (phase 1) and 3.0 s (phase 2). The fuel sulfur contents were 0.85 g/kg (phase 1) and 2.7 g/kg (phase 2). These fuel sulfur contents are modest to high and from a microphysical point of view do not lead to significant differences in the early plume.

The negative ions observed outside and inside the plume are mostly  $\text{NO}_3^-(\text{HNO}_3)_m$  and  $\text{HSO}_4^-(\text{HNO}_3)_m$  with  $m \leq 2$ . The abundance ratio  $R = \text{HSO}_4^-(\text{HNO}_3)_m / \text{NO}_3^-(\text{HNO}_3)_m$  is also shown



**Figure 1.** Time plots of the difference  $\Delta T$  between background and plume temperature (a), and CN-number densities measured by the CN-counter which was integrated into the IOMAS instrument (b). Also given are total negative ion count rates and count rates of ions with  $\text{HSO}_4^-$  and  $\text{NO}_3^-$  cores (d) and their ratio  $R$  (c) measured outside (open symbols) and inside the plume (filled symbols).

in Figure 1 (panel c). Note that only one mean ratio is given for each of the two plume penetration phases 1 and 2. Outside the plume in the "background" atmosphere one finds  $R_B = 0.29 \pm 0.04$  while inside the plume one finds  $R_{P1} = 0.26 \pm 0.13$  (phase 1) and  $R_{P2} = 0.23 \pm 0.10$  (phase 2). Within the uncertainties quoted the above R-values do not significantly differ from each other. This indicates that the ions observed in the plume are entrained ambient atmospheric ions. It also indicates that the entrained atmospheric ions did not "see" sufficiently large gaseous sulfuric acid concentrations to significantly change their composition via reaction (1).

Also depicted in Figure 1 (panel d) are the total negative ion count rate ( $c$ ) and partial count rate for ions with  $\text{NO}_3^-$  and  $\text{HSO}_4^-$ -cores measured by IOMAS. Outside the plume it is  $C_B = 147 \pm 9$  counts/s. Since the ambient ion concentration  $n_B$  at 10400 m is about  $5000 \text{ cm}^{-3}$  [cf. Viggiano and Arnold, 1995] it can be used for "calibration" of the ion detection efficiency of IOMAS. One obtains  $E = C_B/n_B = 0.0294 \text{ counts} \times \text{cm}^3 \times \text{s}^{-1}$ . In the plume one finds  $C_{P1} = 80 \pm 16$  counts/s (phase 1) and  $C_{P2} = 123 \pm 22$  counts/s (phase 2). Within the uncertainties quoted  $C_{P1}$  is significantly smaller than  $C_B$  while  $C_{P2}$  is not. Hence it seems that some modest depletion of entrained ions took place during phase 1 while no significant depletion is found for phase 2.

Interestingly our measurements do not give any direct indication of negative chemiions. Either these have only very small concentrations or must be very massive ( $> 1100$  amu) which would not allow their detection by IOMAS due to its limited mass range (1 - 1100 amu). The latter seems to be the case as will be discussed below.

Using the observed entrained negative ions as probes important plume properties can be inferred (see above). The depletion of entrained ions observed during plume penetration phase 1 indicates that an efficient ion removal process must be at work. Potential processes include ion-attachment to aerosol particles, ion-attachment to water contrail particles and recombination of entrained negative ions with positive chemiions. In a very much simplified view which assumes the total surface area of aerosols ( $A_A$ ) and water contrail particles ( $A_C$ ) as well as the total positive chemiion concentration not to vary with  $t_p$  during the time span which entrained ions spent inside the plume prior to their measurements at  $t_p$  equal to 3.6 and 3.0 s, respectively, one expects the following ion-lifetimes with respect to the above three ion-removal processes:  $t_A = 4/(\beta v A_A)$ ,  $t_C = 4/(\gamma v A_C)$  and  $t_R = 1/(\alpha \text{CI}^*)$ . Here  $\beta$  and  $\gamma$  are sticking probabilities,  $v \approx 2 \times 10^4 \text{ cm/s}$  is the mean thermal ion velocity,  $\text{CI}^*$  is the total positive chemiion concentration, and  $\alpha$  is the ion-ion recombination coefficient which is  $\alpha = 10^{-6} \text{ cm}^3/\text{s}$  for ambient atmospheric ions in the troposphere and lower stratosphere [cf. Viggiano and Arnold, 1995]. However at higher temperatures and for ions having larger masses than such these ions  $\alpha$  should be lower. Since the latter is probably the case for chemiions a range of  $\alpha = 1 \times 10^{-7} - 1 \times 10^{-6} \text{ cm}^3/\text{s}$  is used here. Making the simplifying assumption for ambient atmospheric negative ions to become mixed into the plume at a single  $t_p = t_{PE}$  and to reside in the plume for a time span  $t_{res} = t_{PM} - t_{PE}$  where  $t_{PM}$  is the plume age at which the measurements took place ( $t_{PM} = 3.6$  s for phase 1 and  $t_{PM} = 3.0$  s for phase 2) one obtains:

$$n^-/n_0^- = \exp\left(-t_{res} \times (t_A^{-1} + t_C^{-1} + t_R^{-1})\right) \quad (2)$$

Considering the plume entrainment model recently discussed by Schumann et al. [1997] one crudely estimates  $t_{res} = 2.0$  s (phase 1), and  $t_{res} = 1.7$  s (phase 2). Note that plume edge probing

particularly during phase 2 (see above) may imply that for phase 2 the real  $t_{res}$  was actually smaller than the above estimated 1.7 s.

## Aerosol particles

Using expression (2) the measured  $n^-/n_0^- = c/c_0^- = 0.54$  (phase 1) leads to  $(t_A^{-1} + t_C^{-1} + t_R^{-1}) = 0.31$  for phase 1. This sets a lower limit of 3.26 s for  $t_A$ ,  $t_C$ , and  $t_R$ . With  $t_A = 4/(\beta v A_A)$  and  $\beta = 1.0$  one obtains  $A_A \leq 6.1 \times 10^{-5} \text{ cm}^2/\text{cm}^3$  and with  $t_C > 4/(\gamma v A_C)$  and  $\gamma = 1.0$  one obtains  $A_C < 6.1 \times 10^{-5} \text{ cm}^2/\text{cm}^3$ . Since water contrail particles have typical mean diameters around 300 - 1000 nm which are not anymore small compared to the typical mean free path for ions and molecules  $t_C$  is in fact larger than  $4/(\beta v A_C)$  and hence one obtains  $t_C$  larger than 3.26 s.

The above  $A_C < 6.1 \times 10^{-5} \text{ cm}^2/\text{cm}^3$  may be compared with an  $A_C \approx 1.7 \times 10^{-5} \text{ cm}^2/\text{cm}^3$  which can be inferred from measurements of particles with diameters of 310 nm - 1700 nm made by a forward scattering spectrometer probe FSSP-300 (PMS Inc.) on board of the Falcon [Petzold et al., 1997]. Since this  $A_C$  is markedly smaller than our above  $A_C$  it seems that water contrail particles were not responsible for the ion depletion observed during phase 1.

For aerosol particles only total number densities but no size distributions have been measured on the Falcon. Hence  $A_A$  cannot be inferred from such measurements. When compared with theoretical model calculations of  $A_A$  which are around  $2 \times 10^{-5} \text{ cm}^2/\text{cm}^3$  for sulfuric acid/water-aerosols ( $\epsilon = 0.02$ ) and for  $t_p = 3.5$  s [cf. Yu and Turco, 1997; Danilin et al., 1997]. This corresponds to a total aerosol surface area density of  $3 \times 10^{-5} \text{ cm}^2/\text{cm}^3$ . In comparison our above inferred upper limit  $A_A \leq 6.1 \times 10^{-5} \text{ cm}^2/\text{cm}^3$  is consistent and in fact only somewhat larger. Hence it seems that aerosols may in fact have been responsible for the ion-depletion observed in phase 1. However during phase 2 (large fuel sulfur content) no ion-depletion was observed although soot should be as abundant as in phase 1 and sulfuric acid/water-particles should be more abundant compared to phase 1 due to the larger fuel sulfur content. This puzzling finding seems to argue against soot and sulfuric acid/water-aerosols but may also be explained by less perfect plume penetrations during phase 2 (see above).

## Chemiions

Considering positive chemiions as a potential sink for entrained negative ions in the plume and using the measured  $n^-/n_0^- = 0.54$  one obtains  $t_R \geq 3.26$  s for phase 1. Using  $t_R = 1/(\alpha \text{CI}^*)$  with  $\alpha = 1 \times 10^{-7} - 1 \times 10^{-6} \text{ cm}^3/\text{s}$  one obtains an upper limit for the positive chemiion concentration:  $(\text{CI}^*) \leq 3 \times 10^5 \text{ cm}^{-3} - 3 \times 10^6 \text{ cm}^{-3}$ . In comparison the maximum possible positive chemiion concentration in a plume which is assumed to be limited only by ion-ion recombination is  $(\text{CI}^*) \leq 1/(\alpha t_p)$ . For  $\alpha = 1 \times 10^{-7} - 1 \times 10^{-6} \text{ cm}^3/\text{s}$  and  $t_p = 3.6$  s (phase 1) one obtains  $(\text{CI}^*) \leq 2.8 \times 10^5 \text{ cm}^{-3} - 2.8 \times 10^6 \text{ cm}^{-3}$  [cf. Arnold et al., 1998]. Hence our above inferred upper limit  $(\text{CI}^*) \leq 3 \times 10^5 \text{ cm}^{-3} - 3 \times 10^6 \text{ cm}^{-3}$  (phase 1) is very close to the maximum possible positive chemiion concentration. Negative chemiions should have the same total concentration as positive chemiions. Interestingly the total concentration of negative ions with masses  $< 1100$  amu of  $2500 \text{ cm}^{-3}$  measured by IOMAS in the plume (phase 1) and  $5000 \text{ cm}^{-3}$  (phase 2) are much smaller than the above upper concentration limit for chemiions. Hence if chemiions were indeed as abundant as expected and as indicated by our measurements they must be very massive ( $> 1100$  amu) even for

phase 1 (lower fuel sulfur content). Therefore positive chemiions may in fact also be the cause of the negative ion-depletion observed in phase 1. However no ion-depletion occurred in phase 2 where chemiions should also be present. Hence the absence of ion-depletion for phase 2 is puzzling also in the light of chemiions causing ion-removal. However as mentioned above the absence of ion-depletion for phase 2 may be due to imperfect plume penetrations. Neither aerosols, nor water contrail particles, nor chemiions can explain the difference in ion-depletion for the two phases 1 and 2.

### Gaseous Sulfuric Acid

As mentioned above the absence of a significant change of the measured countrate of ions with  $\text{NO}_3^-$ -cores" in the plume compared to outside the plume sets an upper limit to the gaseous sulfuric acid-concentration (GSA) in the plume:

$$(\text{NO}_3^-)/(\text{NO}_3^-)_0 = \exp(-t_{\text{res}}/t_s) \quad (3)$$

with  $t_s = 1/(k_1(\text{GSA})) = 5 \times 10^8/(\text{GSA})$ . For a conservative smallest  $(\text{NO}_3^-)/(\text{NO}_3^-)_0 \geq 0.5 \pm 0.15$  consistent with our ion composition data one finds  $t_s \geq 2.9 \pm 0.6$  s for phase 1 and  $t_s \geq 2.5 \pm 0.5$  s for phase 2. Hence one obtains  $(\text{GSA}) \leq 1.7 (\pm 0.34) \times 10^8 \text{ cm}^{-3}$  (phase 1) and  $(\text{GSA}) \leq 2.0 (\pm 0.4) \times 10^8 \text{ cm}^{-3}$  (phase 2).

In comparison the total sulfuric acid concentration (SA) of  $3.6 \times 10^9 \text{ cm}^{-3}$  expected for an assumed  $\epsilon = 0.02$  and for phase 2 (fuel sulfur content = 2.7 g/kg) is 18 times larger than our above upper limit  $(\text{GSA}) \leq 2 \times 10^8 \text{ cm}^{-3}$ . It therefore seems that for large fuel sulfur content by far most of the initially formed gaseous sulfuric acid has ended up in the condensed-phase before  $t_{\text{PE}} = 1.3$  s at which most of the observed negative ions became entrained into the plume. Otherwise entrained negative ions should have seen sufficiently large gaseous sulfuric acid-concentrations to remove  $\text{NO}_3^-$ -cores via reaction (1). The lifetime of an  $\text{NO}_3^-$ -core with respect to reaction (1) is  $t_{1S} = 1/(k_1(\text{GSA})) = 5 \times 10^8/(\text{GSA})$  where  $k_1 = 2 \times 10^9 \text{ cm}^3/\text{s}$ . For  $(\text{GSA})$  equal to the expected  $(\text{SA}) = 3.6 \times 10^9 \text{ cm}^{-3}$  (phase 2) one obtains an  $\text{NO}_3^-$ -core ion" lifetime of  $\geq 0.14$  s. The latter is much smaller than  $t_p = 3.0$  s and hence  $(\text{NO}_3^-)/(\text{NO}_3^-)_0$  would be  $\exp(-t_{\text{res}}/t_{1S}) = 5 \times 10^{-6}$ . However the observed  $(\text{NO}_3^-)/(\text{NO}_3^-)_0$  is equal or larger than 0.8.

### Summary and Conclusions

From the preceding discussion the following picture of plume processes emerges: (a) (GSA) initially formed experiences rapid gas-to-particle conversion at plume ages  $\leq 1.6$  s; (b) negative chemiions seem to grow rapidly reaching mass numbers  $> 1100$  amu by  $t_p \approx 3$  s. This growth probably involves  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  clustering and takes place also for the smaller of the two fuel sulfur contents; (c) ambient atmospheric negative ions measured at plume ages of 3.0 and 3.6 s became entrained into the plume at plume ages around 1.3 and 1.6 s and experience only modest depletion in the plume. This depletion seems to be due to ion-attachment to aerosol-particles or due to recombination with positive chemiions.

Future ion composition measurements in exhaust plumes of jet aircraft in flight could include a greatly increased mass range and cover also smaller plume ages. This should allow to detect

chemiions and gaseous sulfuric acid. Also detailed model calculations are required for further interpretations of our experimental data.

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