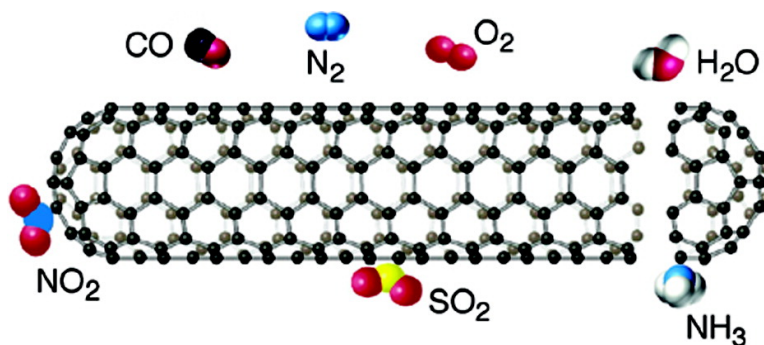


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Single-Wall Carbon Nanotube Interaction with Gases: Sample Contaminants and Environmental Monitoring

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Abstract: Here, we show that residual contaminants in purified single-wall carbon nanotube bundles may be responsible for the reported sensitivity of the electronic and transport properties to oxygen. Removal of these contaminants makes the electronic spectra insensitive to O₂, CO, H₂O, and N₂, while a strong sensitivity to NO₂, SO₂, and NH₃ is observed, confirming the possible application of single-wall nanotubes as powerful sensors capable of measuring environmentally significant levels of toxic gases.

Recent experimental^{1–4} and theoretical^{3–10} works seem to indicate that the transport and electronic properties of single-wall carbon nanotubes (SWCNTs) might change upon exposure to gases such as O₂, NO₂, and NH₃. This observation could have important consequences in practical applications as it could lead to the development of novel gas sensors. On the other hand, it also suggests that the performance of nanotube-based electronic devices may be dependent on the atmospheric environment. Several mechanisms can explain such phenomena. Gas molecules could affect directly the SWCNT properties via physisorption (interaction through van der Waals forces) or chemisorption (formation of chemical bonds), but they could also have an indirect effect by interacting with contaminants bonded to the nanotubes. Therefore, many supposedly intrinsic properties measured on nanotubes may be severely compromised by the presence of extrinsic contaminant molecules.

Using photoemission spectroscopy, we show that the presence of residual contaminants in purified SWCNTs, mainly chemical residues of the purification, dispersion, and filtration processes, is responsible for their claimed sensitivity to oxygen. After complete removal of these contaminants, the electronic spectra of SWCNTs are insensitive to O₂, CO, H₂O, and N₂, while a strong sensitivity to NH₃, NO₂, and SO₂ is confirmed, indicating that SWCNTs are powerful sensors capable of measuring environmentally significant levels of toxic gases.

Purified SWCNTs in the form of bucky-paper (1 × 1 cm²) with stated purity >90% vol, obtained according to the purification procedure described by Monthieux et al.¹¹ for sample #3, were inserted in an ultrahigh-vacuum experimental chamber (base pressure 10^{–10} mbar) via a fast-entry-lock. The measurements were performed at the SuperESCA beamline of the ELETTRA synchrotron facility, with the sample mounted on a manipulator that allows cooling to 150 K and annealing up to 1800 K. Before and after all of the treatments described hereafter in the text, the sample was checked using electron energy loss spectroscopy (EELS), performed in situ with a monochromated electron gun (energy resolution 70 meV),¹² and ex situ with Raman spectroscopy.¹³ No changes were observed in both EELS and Raman spectra, confirming that after the ultrahigh-vacuum treatments the SWCNTs, with an average diameter of 1.3 ± 0.1 nm, were still intact without detectable graphitic material.

The chemically selective core level photoemission spectroscopy identified several contaminants in the pristine bucky-paper. These contaminants remained in the sample even after annealing cycles at 1075 K in ultrahigh vacuum. In particular, after these annealing cycles, we found a large amount of Na, likely a residual of the surfactant (sodium lauryl sulfate) and of the NaOH bath, catalyst particles (Ni in our case), and a small photoemission signal coming from the oxygen species. As expected from the purification procedure,^{11,14} minor quantities of other impurities, Si and S, were observed as well. However, as we will show elsewhere using photoemission microscopy and X-ray emission microscopy,¹³ the Si and S impurities do not affect the properties of SWCNTs because they are not bonded

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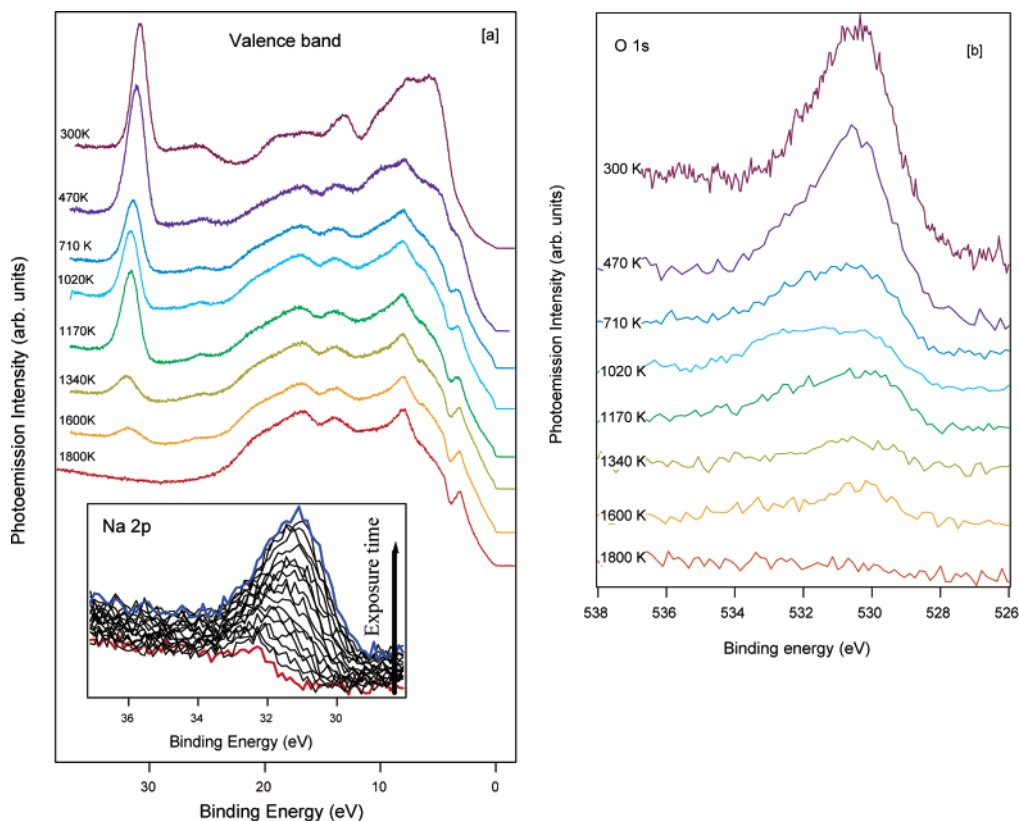


Figure 1. (a) Valence band photoemission spectra of the bucky-paper sample at subsequent increasing flashing temperatures. Note the reduction and final disappearance of the Na 2p core level peak at ~ 31.5 eV. Inset: Increasing Na 2p photoemission signal with time when the sample flashed at 1800 K was irradiated with the 90 eV photon beam. (b) O 1s core level photoemission spectra of the bucky-paper sample at subsequent increasing flashing temperatures.

to the carbon atoms, and after the annealing treatments they form solely isolated clusters.

The evolution of the valence-band photoemission spectra of the SWCNT bucky-paper as a function of annealing cycles at increasing temperatures (1 minute of annealing time for each temperature reported) is shown in Figure 1 (the inset of which will be explained later in the text). The spectral region extends up to 40 eV, including therefore also the Na 2p core level signal, visible as a sharp peak at ~ 31.5 eV of binding energy.

As the annealing temperature increases, the Na 2p signal gradually diminishes, and a distinct emission appears at the Fermi level (binding energy of 0 eV). The Fermi edge is not related to the SWCNTs electronic structure, but is due to the presence of Ni particles diffusing toward the surface. Indeed, core level photoemission indicates that the complete removal of the Ni particles is obtained by flashing the sample at 1800 K, and, correspondingly, the Fermi edge disappears from the valence band spectrum (see the bottom spectrum of Figure 1). The flash at 1800 K apparently also removed the sodium-containing and oxygen contaminants, as is manifested by the disappearance of the Na 2p and O 1s core level signals.

By exposing this flashed sample to molecular oxygen at 150 K, we observed a strong effect on the C 1s core level. As shown in Figure 2, during the exposure, the C 1s core level gradually shifted to lower binding energies, narrowing the line width. Simultaneously, a peak appeared in the photoemission binding energy region where the O 1s emission is expected, its intensity increasing with O₂ exposure. These changes in the photoemission spectra were completely reversible: by annealing the sample, mass selected thermal desorption spectra and O 1s

photoemission spectra indicated that oxygen was released, and, correspondingly, the C 1s spectrum evolved toward its initial shape and binding energy. Because the physisorption probability of molecular oxygen on SWCNTs in ultrahigh-vacuum conditions is practically null above 100 K, the released oxygen should be (weakly) chemisorbed.¹⁵ The changes observed in the C 1s core level during the oxygen exposure might be associated to a charge transfer from the carbon system to the bonded oxygen and apparently confirm the results of Collins et al.,¹ suggesting a strong sensitivity of the SWCNT electronic properties to O₂. As we will describe below, however, this is incorrect, and the observed behavior is an artifact mainly induced by sodium-containing species still present in the bulk bucky-paper.

Indeed, after the above oxygen cycles, a small Na 2p signal surprisingly reappeared in the valence band photoemission spectra (red curve in the inset of Figure 1). We also realized that the Na 2p signal was increasing while exposing the sample to the X-ray beam, as shown in the inset of Figure 1. A new flash at 1800 K removed the Na 2p photoemission signal, but the Na 2p peak slowly reappeared under the exposure to the 90 eV X-ray beam. This behavior clearly indicates that chemical species containing sodium are still present in the bucky-paper within the volume probed by the soft X-rays, which is bigger than the volume probed by photoelectrons. These chemical species probably dissociate under the intense synchrotron beam, and the released sodium can diffuse toward the surface.

The complete removal of the Na contamination was obtained only after annealing the bucky-paper at 1270 K for several hours.

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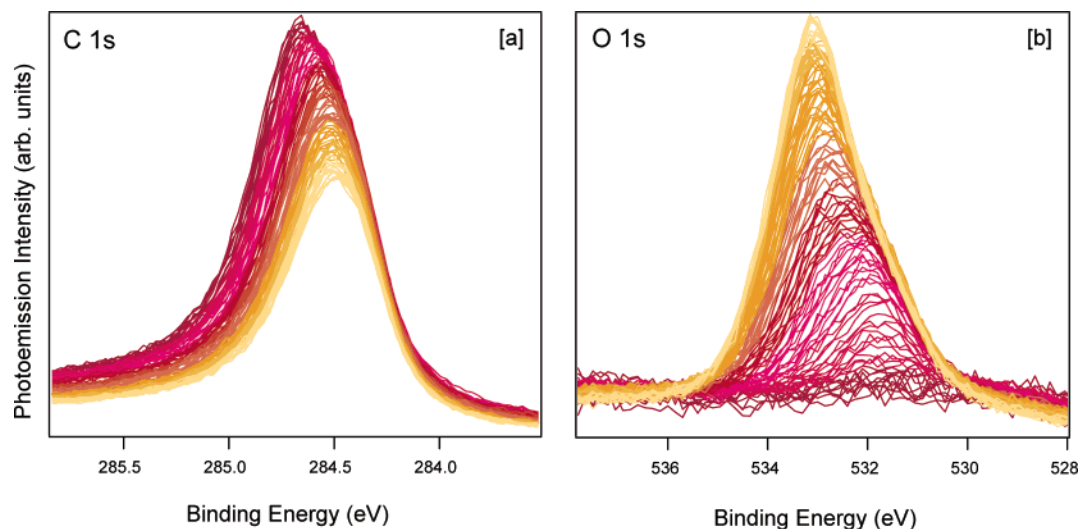


Figure 2. C 1s (a) and O 1s (b) spectra of the bucky-paper flashed at 1800 K measured while exposing the sample at 150 K to O₂ at a partial pressure of 10⁻⁷ mbar. The acquisition time is 40 s per spectrum.

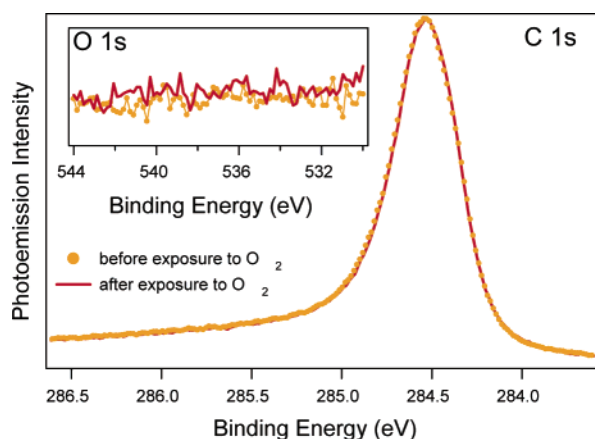


Figure 3. C 1s spectra of the clean SWCNT bucky-paper (see text for definition) before and after exposure at 150 K to thousands Langmuir of O₂ at a partial pressure of 10⁻⁶ mbar. Inset: Spectral region where the O 1s emission should be expected.

After contaminant elimination, the clean sample was cooled at 150 K and exposed to various gas molecules, while monitoring the valence band and core level photoemission spectra. In the case of CO, N₂, H₂O, and O₂, no effects on the carbon-derived photoemission features were observed using a gas partial pressure of the order of 10⁻⁶ mbar and exposures of several thousands of Langmuir (L). In Figure 3, for example, we show the C 1s core level of the clean sample before and after the exposure to 10⁵ L of O₂. The spectrum remained absolutely unchanged after the exposure to oxygen (the same was true for the valence band photoemission spectrum), and, as shown in the inset, no O 1s core level peak, indicative of adsorbed oxygen species, was observed. The same happened for the exposure to N₂ and CO. In the case of H₂O, obviously ice formed at 150 K on the sample, but the line shape and binding energy of the C 1s core level remained unaffected while dosing water, apart from the reduction of photoemission intensity due to the growing ice layer. It is worth noting that the C 1s spectrum of this sample remained unaffected also after air exposure at atmospheric pressure at both room and lower temperatures.

The above observations indicate that N₂, CO, H₂O, and O₂ interact with clean SWCNTs via weak dispersion forces only and do not affect the electronic spectra (properties) of SWCNTs.

In the particular case of O₂, this observation contrasts with the experiment of Collins et al.¹ and with some theoretical investigations,⁵ but agrees with more recent experiments¹⁵ and calculations.¹⁶ A possible explanation is that the observed strong sensitivity of SWCNT properties to oxygen reported in ref 1 was induced by the presence of contaminants (likely Na-containing molecules), as observed in the present experiment before the complete removal of the contaminants. A further possibility is that oxygen may be chemisorbed at defect sites and open tube caps where dangling bonds are present. Indeed, in our case, according to Monthieux et al.,¹¹ the ultrahigh-vacuum high-temperature annealing strongly reduces the number of defects introduced by the purification treatments, restoring the nanotube structure and the bundle network, and should also close the nanotube caps. These phenomena may be the reason for the observed insensitivity to oxygen after the prolonged annealing in ultrahigh-vacuum conditions.

It is also worth noting that, in recent papers,^{17,18} Avouris and co-workers studying SWCNT field-effect-transistors, formed by a single tube, observed that the absorption of oxygen at the nanotube/metal junction influences the transport properties of the nanotube device and suggested this mechanism as an explanation for the results of ref 1. However, Collins et al.¹ measured nanotube bundles and thin films, instead of an isolated single nanotube, and the effect of the nanotube/metal junction in this systems may be negligible or comparable to the effect induced by the chemisorption of oxygen on contaminant species bonded to the nanotubes.

In contrast to the case of oxygen, the exposure of the clean SWCNT sample to NH₃, NO₂, and SO₂ molecules was accompanied by clear changes in the carbon photoemission features. These changes reflect new carbon chemical surroundings and sizable charge redistribution between the adsorbed species and the SWCNTs. Figure 4a–c shows the C 1s spectra measured in real-time with fast-photoemission (40 s per spectrum) during the exposure to SO₂, NH₃, and NO₂, respectively. In all three cases, the C 1s peak shifts and changes shape

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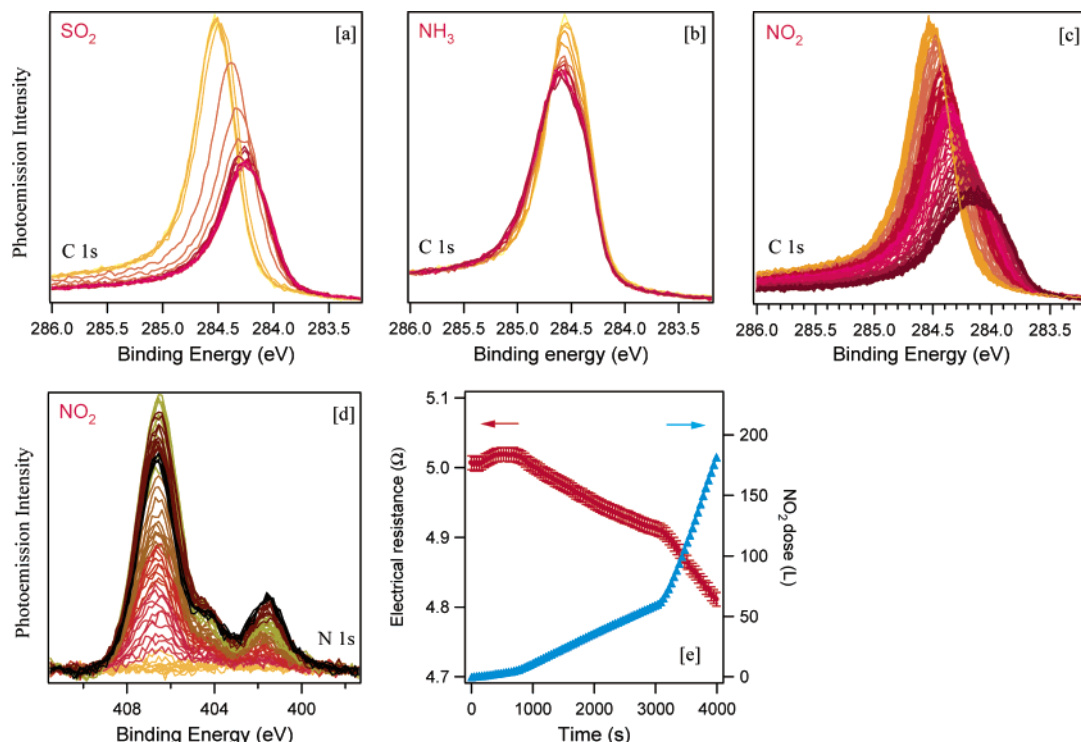
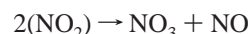


Figure 4. C 1s spectra of the clean SWCNT bucky-paper measured while exposing the sample at 150 K to SO₂ (a), NH₃ (b), and NO₂ (c) at partial pressures of about 10⁻⁸ mbar. In the case of NO₂, the evolution of the N 1s (d) spectra is also shown. (e) SWCNT bucky-paper resistance (red dots) as a function of NO₂ dose (blue triangles) at 150 K.

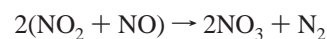
as the exposure time increases. The shift is toward lower binding energy and of comparable size in the case of NO₂ and SO₂. In the case of NH₃, the shift is smaller and on the opposite side, that is, toward higher binding energies. If these binding energy shifts are ascribed to shifts of the nanotube chemical potential, the NO₂ and SO₂ molecules bound to SWCNTs act as charge acceptors, while the NH₃ molecules act as charge donors. These observations are in full agreement with those reported by Kong et al.² and with recent calculations.^{8,9}

For the case of NO₂, we also show in Figure 4d,e the N 1s photoemission spectra and the SWCNT sample resistance, measured with a two-probe system, taken while exposing the sample to the gas. The N 1s photoemission spectra show the presence of three peaks at about 401.5, 404.5, and 407 eV. Because at 150 K the nitrogen oxides do not form multilayer films at an ambient pressure lower than 10⁻⁵ mbar, the observed N 1s peaks have to be ascribed to molecular species bonded to the SWCNTs. NO₂ is a molecule that can undergo complex transformations interacting with surfaces: it can dimerize, disproportionate, decompose, or react to form NO₃, NO, and N₂O species. Systematic studies of NO and NO₂ adsorption on metal^{19,20} and oxide surfaces^{20–23} indicate that the low binding energy component (401.5 eV) is due to NO species, while the component at 404 eV can be associated to a small fraction of NO₂ molecules and the most intense peak at 407 eV to NO₃ species. Because N 1s spectra similar to that reported in Figure 4d, that is, having a similar ratio between the three peak

intensities, are observed in different sample positions after this adsorption experiment (i.e., sample regions not illuminated by the 200 × 30 μm² beam spot while dosing the gas) or after NO₂ adsorption experiments in the absence of photon beam, these oxide species are not produced by photoinduced reactions, but can be associated to the dissociation, disproportion, and reaction of NO₂ molecules interacting with SWCNTs. NO₂ is known to interact with catalytic surfaces to form NO and NO₃ according to the following reaction:^{19–23}



This reaction implies a 1:1 ratio between NO and NO₃ species, while from our experiments it is clear that the formation of NO₃ species is dominant. A possible explanation is that the adsorption coefficient for NO is lower than that for NO₃ and part of the NO molecules are released as gas. However, a further pathway to explain this observation is also the occurrence of the following reaction:



where the N₂ molecules do not adsorb on SWCNTs, in agreement with the above adsorption experiments of N₂ and the absence of N 1s peaks below 400 eV of binding energy in the photoemission spectra.

The bucky-paper resistance decreases as the exposure to NO₂ increases, in agreement with the observation of Kong et al.² Changes in the partial pressure of NO₂ (i.e., changes in the slope of the blue curve) are directly reflected in the slope of the resistance curve, confirming that the resistance decrease is directly related to the adsorption/reaction of NO₂ molecules on the SWCNT surface. Both core level and resistance measurements indicate that clear variations in the electronic and transport

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properties of SWCNTs are detectable well above the noise level after exposing the sample to 40 L of NO₂. A similar response of the core level is observed in the case of SO₂ and NH₃. An exposure of 40 L means an exposure to a partial pressure of 10⁻⁵ mbar (i.e., 10 ppb of toxic molecules in air at atmospheric pressure) for about 4 s. In other words, SWCNT bundles at 150 K are able to feel the presence of 10 ppb of toxic gas in air in 4 s. For comparison, a typical solid-state sensor based on conducting polymers can detect a few ppm of NO₂, SO₂, or NH₃ by a typical response time of 1 min at room temperature,²⁴ while detectors based on In₂O₃ and SnO₂ are sensitive to 30–100 ppb of NO₂ with a typical response time longer than 1 min.²⁵

Finally, we note that all of the observed changes in the electronic spectra and transport properties of SWCNTs exposed to NH₃, NO₂, and SO₂ are completely reversible by annealing the SWCNT sample above 800 K in UHV.

In conclusion, our experimental results confirm that SWCNTs could find use as powerful chemical gas sensors capable of measuring environmentally significant levels of toxic molecules (i.e., <100 ppb) such as SO₂, NH₃, and NO₂, but likewise

indicate that many supposedly intrinsic properties measured on as-prepared or mildly annealed in a vacuum purified nanotubes may be severely compromised by the presence of catalyst particles, contaminants, and defects coming from the purification procedure. In particular, our results strongly suggest that gas molecules present in air (e.g., O₂, H₂O, and N₂) interact weakly with SWCNT bundles, through dispersion forces only and not by the formation of even weak chemical bonds. We observe that the electronic structure, as reflected in the photoemission spectra (and likely the transport properties), of clean SWCNTs at 150 K is not influenced by the exposure to these molecules. This conclusion is quite important for future applications of SWCNTs in electronics because it suggests that the performances of nanotube-based devices should not be influenced by the air exposure.

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