Dramatic differences in carbon dioxide adsorption and initial steps of reduction between silver and copper

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Converting carbon dioxide (CO₂) into liquid fuels and synthesis gas is a world-wide priority. But there is no experimental information on the initial atomic level events for CO₂ electro-reduction on the metal catalysts to provide the basis for developing improved catalysts. Here we combine ambient pressure X-ray photoelectron spectroscopy with quantum mechanics to examine the processes as Ag is exposed to CO₂ both alone and in the presence of H₂O at 298 K. We find that CO₂ reacts with surface O on Ag to form a chemisorbed species (O = CO₂δ−). Adding H₂O and CO₂ then leads to up to four water attaching on O = CO₂δ− and two water attaching on chemisorbed (b-)CO₂. On Ag we find a much more favorable mechanism involving the O = CO₂δ− compared to that involving b-CO₂ on Cu. Each metal surface modifies the gas-catalyst interactions, providing a basis for tuning CO₂ adsorption behavior to facilitate selective product formations.
n order to close the anthropogenic carbon circle while creating a sustainable hydrocarbon-based energy cycle, it is essential to discover new electrocatalysts that can efficiently convert carbon dioxide (CO$_2$) into liquid fuels and feedstock chemicals$^{7-11}$. However, CO$_2$ is highly inert, making the CO$_2$ reduction reaction (CO$_2$RR) unfavorable thermodynamically. High throughput experimental and computational screening methods have been employed to discover new advanced CO$_2$ reduction catalysts, but these approaches are based on preconceived notions of the reaction mechanisms and have not produced dramatic successes$^{8-11}$. To accelerate progress we believe that it is essential to develop a complete atomistic understanding of how CO$_2$ interacts with and is transformed by the catalyst surfaces to provide guidance to design the catalyst to selectively tune the mechanisms for adsorption and activation.

Electrocatalysts such as Au, Ag, Zn, Pd, and Ga are known to yield mixtures of CO and H$_2$ at varying ratios depending on the applied voltage$^{12-16}$, with Ag exhibiting particularly high activity and selectivity to CO vs. H$_2$. We sought to obtain a comprehensive understanding of how CO$_2$ and H$_2$O molecules adsorb on the Ag surface and interact to initiate CO$_2$ dissociation and subsequent product formation.

Here we report our findings combining in-situ ambient pressure X-ray photoelectron spectroscopy (APXPS) with quantum mechanics (QM), which leads to unexpected and exciting findings for CO$_2$ surface adsorption on Ag surface that are quite different than observed previously for Cu surfaces. We find that physically adsorbed linear (-) and chemisorbed bent (-) CO$_2$ are not stable on pure Ag (111) surface, but rather gaseous (-) CO$_2$ reacts with on-top surface oxygen (O) atoms on Ag to form a chemisorbed species (O=CO$_2$). This surface species stabilizes up to four adsorbed H$_2$O through forming hydrogen bonds (HBs). We also find that a pair of surface H$_2$O stabilize b-CO$_2$ on the Ag by forming two HBs between the H$_2$O$_{ads}$ and CO$_2$. The QM results and experimental observations suggest that the (O=CO$_2$)-(H$_2$O)$_n$ clusters are the main surface adsorbates on CO$_2$ and H$_2$O co-adsorption. On Ag we find a very different and more favorable mechanism of activating CO$_2$, involving the O=CO$_2$δ−, compared to that involving b-CO$_2$ on Cu. Ag and Cu surfaces differ in both the chemical speciation and the respective adsorption energies, operating entirely differently for the first step of activating CO$_2$.

CO$_2$ adsorption on Ag surfaces. The (111) surface is closest packed, making it the most favorable facet for Ag and Cu. Indeed experimental evidence shows that silver (and Cu) at high temperature exposes this facets$^{17,19,20}$. Thus our simulations compare results on the Ag (111) surface with experimental observations on vacuum annealed polycrystalline Ag surface.

We started by carrying out QM studies to examine the stability of various surface adsorbates on pristine Ag surfaces, considering both l- and b- CO$_2$. The optimized structure for l- and b- CO$_2$ is found to be unfavorable with $E_{ads}$ (QM electronic binding energies) = −0.15 eV and ΔG = +0.19 eV, and $E_{ads}$ = +0.77 eV and ΔG = +1.13 eV, respectively (Supplementary Fig. 2). These and all other ΔG values are from QM calculations including zero point energy, entropy, and specific heat to obtain ΔG at 298 K and at the pressure quoted.

CO$_2$ adsorption on oxygen treated Ag surfaces. We started the calculation by considering the possible promotion effect of sublayer oxygen that we found previously to stabilize CO$_2$ adsorption on Cu surface. However, for Ag the QM finds that subsurface O minimizes to the O at the surface. In the presence of isolated surface O, we found that l-CO$_2$ has ΔE$_{ads}$ = −0.21 eV, but ΔG = +0.13 eV (Supplementary Note 2; Supplementary Fig. 2). Thus a pressure of ~30 Torr would be required to stabilize l-CO$_2$ on the O/Ag surface at 298 K.$^5$ This contrasts with observations for Cu, where subsurface O stabilized the adsorption of l-CO$_2$ on Cu surface under 0.7 Torr CO$_2$ partial pressure at 298 K.$^5$ (Fig. 1b). This attraction resulted from the subsurface O in a tetrahedral site inducing Cu$^+$ character into the single Cu atom above it on the surface, which stabilized the l-CO$_2$. This oxygen promotion effect is not observed for Ag because the O is chemisorbed on top of the Ag, which does not facilitate Ag oxidation (to Ag$^{2+}$)$^{19,21-25}$. This contrasting result provides fresh insight into the tunability of CO$_2$ adsorption on metal surfaces. We evaluated the stabilization of b-CO$_2$ next to surface O$_{ads}$ on Ag, but the QM minimizes to form a surface carbonic acid-like species (Supplementary Fig. 2) with a C=O$_{up}$ double bond (1.222 Å) pointing up while the other two O bind to adjacent three fold Ag (111) sites with C-O lengths of 1.365 Å and 1.354 Å and O-Ag distances of 2.276 Å (Fig. 2a). This is not an ionic carbonate possessing three similar O atoms, as had been speculated previously$^{26-28}$. The CO$_2$ binding energy to form surface O=CO$_2$δ− is ΔE$_{ads}$ = −0.75 eV, ΔG = −0.28 eV. We denote this carbonic acid-like adsorbate as O=CO$_2$δ− to indicate that the negative charge is on the two O binding to the Ag surface. The total charge of O=CO$_2$δ− is −1.26e− and charge on C is +1.46, leading to C 1s binding energy (BE) of −269.45 eV. The simulated BE value corresponds to 287.9 eV in the experimental observation (Fig. 2b). The configuration of the O=CO$_2$δ− illustrated in top view is shown in Supplementary Fig. 3. The properties of the surface O=CO$_2$δ− are summarized in Supplementary Note 3, and Supplementary Figs. 4 and 5. The simulated vibrational frequency data for O=CO$_2$δ− are summarized in Supplementary Table 2.

We also investigated structures with vertical and horizontal CO$_2$ configurations on the Ag (111) surface (Supplementary Fig. 6). We find that the structure with one O bridging to the
surface and two C–O bonds pointing up is not stable with $E_{\text{ads}} = +0.32$ eV. This starting structure rotates to form the stable bidentate species. We also examined the stability of the horizontal CO$_3$ configuration with three C–O bonds constrained to be parallel to the Ag surface. This configuration is not stable. The CO$_2$ bonding energy to form this horizontal structure is $\Delta E_{\text{ads}} = -0.34$ eV, $\Delta G = +0.13$ eV. Moreover, the adsorption of CO$_2$ on the Ag (111) surface with an Ag vacancy induced by oxygen adsorption was examined and found to be unstable on this structure (Supplementary Fig. 7).

The adsorption states of CO$_2$ on various Ag surfaces at 298 K were monitored by C 1 s APXPS. The pristine Ag surface shows no detectable carbon- and oxygen-based contamination (Supplementary Fig. 8), while dosing O$_2$ under different experimental conditions results in various oxygen coverages on Ag surface, that we monitor via the changes of the O$_\text{ad}$ peak intensity (the detailed characterizations of the surface are shown and discussed in Supplementary Note 4 and Supplementary Figs. 9 and 10).

We partition the C 1 s spectra obtained on clean and oxygen-covered Ag surfaces into two parts. First, high binding energy region from 286–290 eV, showing the surface adsorbate, O = CO$_2$$^\delta^-$ at 287.9 eV. O = CO$_2$$^\delta^-$ is the only stable species on the Ag surface when exposed solely to CO$_2$ (no H$_2$O is present), leading to a single C 1 s peak in the adsorbate signal region of the APXPS spectra (Fig. 2b and Supplementary Fig. 11). Second, low binding energy region from 282 eV to 286 eV represents the surface reaction products from possible reactive carbon compounds (e.g., unsaturated hydrocarbons) from the chamber. The chemical species can be assigned as atomic C or carbide (283.0 eV), sp$^2$ C = C (284.2 eV), sp$^3$ C–C (285.2 eV), and C–O (H) (286.0 eV)$^{29-32}$ (Supplementary Fig. 12).
0.3 Torr CO₂

1s APXPS spectra for Ag surfaces in the presence of 0.3 Torr CO₂ at 298 K. One single C 1s peak representing O structures for O=CO₂− stabilized by a pair of H₂O ad each forming a HB with an O of H₂O on this site with ΔG of −0.18 eV, lower than the O=CO₂− without considering the signal decay due to introducing gases. The peak intensity is the raw intensity point used for the eye guidance. The peak intensity is the raw intensity without considering the signal decay due to introducing gases.

Fig. 2 The QM predictions and experimental observations of Ag surface with CO₂ adsorption alone and in the presence of H₂O at 298 K. a Predicted structures for O=CO₂− on Ag surface. The O=CO₂− C 1s peak BE has been set as the reference point for subsequent experiments with H₂O. b The C 1s APXPS spectra for Ag surfaces in the presence of 0.3 Torr CO₂ at 298 K. One single C 1s peak representing O=CO₂− was observed. c b-CO₂ becomes stabilized by a pair of H₂O ad each forming a HB with an O of b-CO₂ leading to ΔG of −0.18 eV with respect to desorbing H₂O and CO₂. d, e The adsorbed O=CO₂− species stabilizes one or two H₂O ad via HBs to the O ad and two more water with HBs to the O up. O=CO₂− stabilizes the 1st, 2nd, 3rd, and 4th H₂O on this site with ΔG of −0.41 eV, −0.45 eV, −0.37 eV, and −0.19 eV, respectively. f The C 1s APXPS spectra and the peak deconvolution results for Ag surfaces in the presence of 0.3 Torr CO₂ and 0.15 Torr H₂O at 298 K. This deconvolution used the peak separations from the theory. The new surface adsorbates, (O=CO₂−)-(H₂O)₁,₂ and (b-CO₂)-(H₂O)₂, are observed experimentally in the APXPS measurements, showing up as the two new peaks at 0.4 eV and 0.8 eV, lower than the O=CO₂− peak. The species (O=CO₂−)-(H₂O)₃,₄ do not lead to additional peaks, because they are located at position that overlaps with that of O=CO₂−.

Fig. 3 The C 1s signal of surface adsorbate increase as a function of CO₂ dosing time. The adsorbate signals for 0.3 Torr CO₂ adsorption alone and in the presence of 0.001 Torr O₂ were recorded at an increased dosing time, shown as red and blue points, respectively. A black line across the data point is used for the eye guidance. The peak intensity is the raw intensity without considering the signal decay due to introducing gases.

Fig. 13. The largely accelerated process for the surface to reach equilibrium by adding O₂ is due to the formation of surface oxygen. Since CO₂ adsorption on clean (non-oxygen pretreated) Ag surface requires a CO₂ dissociation process prior to the formation of the final surface adsorbate, the dynamics of O=CO₂− formation on clean Ag surface is slower than that with the oxygen co-dosed.

It is well known that during ambient pressure exposure of CO₂, possible residual reactive carbon compounds (e.g., unsaturated hydrocarbons) can be desorbed from the chamber. Thus, due to the slow surface reaction of CO₂ on the clean Ag surface could lead to a larger possibility for the Ag surface to be exposed to unsaturated hydrocarbons that can lead to the formation of the sp² carbon species. After the surface acquires surface O ad (Supplementary Fig. 9) or is co-dosed with O₂ (Fig. 3), CO₂ can react directly on the surface to form O=CO₂−. This suppresses surface carbon formation as evident in the decrease of the surface carbon (mainly the sp² C=C(CO₂−)₃) C 1s signals (Supplementary Fig. 12), resulting in more available surface sites to increase the amount of adsorbed O=CO₂− (Fig. 3 and Supplementary Fig. 11).

In addition, we made an estimate of the surface coverage by calculating the Ag and O atomic ratio, and the O=CO₂−:Agsurf ratio.
ratios, which we found to be around 0.4:1, 0.6:1, and 0.7:1. This indicates that the reaction between surface O and Ag to form \( \text{O} = \text{CO}_2 \delta^- \) happens at surface majority sites, justifying the use of the Ag (111) model in the this study.

**CO\textsubscript{2}** adsorption on Ag surfaces in the presence of H\textsubscript{2}O. The QM studies find that the \( \text{l-CO}_2 \) configuration on Ag surface is not stable even considering the possible promotion effects of both O\textsubscript{ad} and adsorbed water (H\textsubscript{2}O\textsubscript{ad}) (Supplementary Fig. 2). Adding H\textsubscript{2}O to the surface with \( \text{O} = \text{CO}_2 \delta^- \) formed from g-CO\textsubscript{2} leads to two groups of structures stable at 298 K and the applied pressures (Fig. 1d). First, a pair of surface H\textsubscript{2}O stabilizes b-CO\textsubscript{2} on the Ag surface by forming two HBs between the H\textsubscript{2}O\textsubscript{ad} and CO\textsubscript{2} (Fig. 2c). Second, O = CO\textsubscript{2}δ− can stabilize up to 4 H\textsubscript{2}O molecules through formation of HBs to the surface bonds of \( \text{O} = \text{CO}_2 \delta^- \). The 1\textsuperscript{st} and 2\textsuperscript{nd} H\textsubscript{2}O\textsubscript{ad} each forms a HB to one O\textsubscript{ad} bonded to the surface (Fig. 2d), while adding the 3\textsuperscript{rd} and 4\textsuperscript{th} H\textsubscript{2}O force the C = O\textsubscript{op} bond to rotate from being perpendicular to the surface to being nearly parallel to the surface, allowing the formation of HB from a 3\textsuperscript{rd} and 4\textsuperscript{th} surface H\textsubscript{2}O\textsubscript{ad} to the two sp\textsuperscript{3} lone pairs on the C = O\textsubscript{op} unit (Fig. 2e and Supplementary Figs. 3 and 4). From QM predictions, the 1\textsuperscript{st} and 2\textsuperscript{nd} H\textsubscript{2}O\textsubscript{ad} shift the C 1s from −269.45 eV to −269.09 eV and −269.15 eV, while the 3\textsuperscript{rd} and 4\textsuperscript{th} H\textsubscript{2}O\textsubscript{ad} shift the C 1s back to −269.34 eV and −269.50 eV, nearly the same BE’s as for no H\textsubscript{2}O\textsubscript{ad} bonding (Fig. 2f and Supplementary Fig. 5). Considering that the O = CO\textsubscript{2}δ− and surface water stabilize each other through HB, an increase in the surface adsorbate coverage when dosing CO\textsubscript{2} in the presence of surface water stabilize each other through HB, leading to a similar amount of charge transferred directly from the adsorbed CO\textsubscript{2} alone (Supplementary Figs. 11 and 12). This work highlights that the charge transfer con

Proposed CO\textsubscript{2} reduction reaction pathway on Ag and Cu. The CO\textsubscript{2} adsorption on Ag contrasts dramatically from the results on Cu (Supplementary Table 3) providing possible explanations for why these metal catalysts have very different CO\textsubscript{2} reduction performances. For Cu our full explicit solvent QM calculations for the initial step of CO\textsubscript{2} to CO found that hydrogen bonding with the explicit solvent forms a similar b-CO\textsubscript{2} stabilized by two surface H\textsubscript{2}O\textsubscript{ad}. In that case, the next step is for one of these two H\textsubscript{2}O molecules to transfer an H to form the HOCO intermediate plus OH\textsubscript{ad} and then a second surface H\textsubscript{2}O transfers an H to the OH of HOCO to form H\textsubscript{2}O plus OH\textsubscript{ad}, leading to CO\textsubscript{ad} (this general reaction pathway is depicted in Fig. 5a).

For Ag with (b-CO\textsubscript{2}−)-(H\textsubscript{2}O)\textsubscript{n}, Fig. 5a shows that the QM predicted free energy barrier is 0.99 eV on Ag for protonating the complex of b-CO\textsubscript{2} with two H\textsubscript{2}O to form HOCO* plus OH* and H\textsubscript{2}O (Supplementary Fig. 14), leading to a total barrier of hydrogenation of CO\textsubscript{2} to HOCO* of (−0.18) + (0.99) = 0.01 eV (Fig. 5a). This energy barrier is comparable to that on Cu, which is 0.80 eV\textsuperscript{37}

Surprisingly for Ag with (O = CO\textsubscript{2}δ−)-(H\textsubscript{2}O)\textsubscript{n} clusters we find a different mechanism that is significantly more favorable. The discovery that (O = CO\textsubscript{2}δ−)-(H\textsubscript{2}O)\textsubscript{n} is a stable surface cluster is most unprecedented, differing dramatically from our previous understanding of CO\textsubscript{2} on a metal surface, which essentially all involve (b-CO\textsubscript{2}−)-(H\textsubscript{2}O)\textsubscript{n} configurations\textsuperscript{38–42}.

We used QM to discover the mechanism of activation for the carbonic acid-like species on Ag. We find that the first step is for the H\textsubscript{2}O hydrogen bonded to the surface O to transfer an H to form the (C = O)(O)(OH) intermediate plus OH\textsubscript{ad}, as shown in Fig. 5b. The QM energy barrier is 0.62 eV, which is dramatically lower than the value of 0.80 eV for Cu, perhaps explaining the faster rate for Ag. Thus the barrier of hydrogenation of CO\textsubscript{2} to OCOOH* of (−0.28) + (−0.41) + (−0.45) + (0.62) = −0.52 eV (Fig. 5b and Supplementary Fig. 14). This energy barrier is much smaller than for Cu. In particular, it is important to note that the energy levels of all the reaction steps starting with O = CO\textsubscript{2}δ− are negative. This suggests that we might be able to see this reaction in APXPS by simply increasing the temperature. These results predict that the most energetically favorable reduction reaction pathway to hydrogenate CO\textsubscript{2} to HOCO* involves the O = CO\textsubscript{2}δ− configuration present only on Ag surface. This process is unprecedented and has never even been previously speculated. This result raises numerous questions about subsequent steps that will drive many new experimental and theoretical studies to determine the implications. Future studies will include the operando spectroscopic characterizations of these adsorbates under external potentials, and we will predict the Tafel slope to compare with previous experimental observations and to gain more insights into the new mechanism.

**Discussion**

Our studies have established a comprehensive but totally new picture of the first steps of CO\textsubscript{2} activation on Ag. The dramatic
differences with Cu show how interactions between adsorbate and catalyst can be altered by tuning the charge transfer between them through changing the adsorption sites, configuration, and by introducing surface co-dosing adsorbates. These findings provide fresh insights about CO$_2$ adsorption species and the initial steps of CO$_2$ reduction mechanism on Ag surfaces. It is dramatically different from those on Cu surfaces, where $l$-CO$_2$ leads to $b$-CO$_2$ and then directly to CO$_2$ reduction.32.

Using synergistic experimental and theoretical analyses, we find that surface O (from O$_2$ pre-dosing and CO$_2$ self-decomposition) interacts with $g$-CO$_2$ to form a carboxylic acid like intermediate O = CO$_2$$^{δ-}$, the only stable species on Ag surface (exposed to CO$_2$ only). Adding H$_2$O and CO$_2$ then leads to attaching up to four water on O = CO$_2$$^{δ-}$, which for Cu is the intermediate on the way to forming CO. On Ag we find a very different and much more favorable mechanism involving the O = CO$_2$$^{δ-}$, one that has not been suggested or observed previously. This raises numerous questions about the subsequent steps that could motivate the exploration of new chemistries.

Fig. 4 The electronic properties of various surface adsorbates on Ag and Cu. The charge distribution on the C, O and the adsorbate are summarized, with the corresponding C 1 s BE revisited. The various configurations of the adsorbate on the surface modify the charge transfer process, leading to different charge distribution on the adsorbates. Compared to $l$-CO$_2$ (only observed on Cu surface), CO$_2$ in the bent configuration exhibits extra charge accumulation. b-CO$_2$ is stabilized on Ag only with two surface H$_2$O but the charge distribution is similar to $b$-CO$_2$ on Cu surface. However, their different distances to the Ag and Cu surface lead to different C 1 s peak BE’s. With the formation of the first two HBs to surface H$_2$O, the total charge on O = CO$_2$$^{δ-}$ decreases, which decreases the C 1 s BE by -0.30 eV. But adding the 3rd and 4th H$_2$O with HB to the C = O$_{ag}$ of the O = CO$_2$$^{δ-}$ increases the charge, shifting the BE back to 0.05 eV above the peak for no H$_2$O. Thus the predicting C 1 s shifts and charge distribution on surface adsorbates are fully consistent with the experimental observed C 1 s BEs. These observed differences show the tunability of CO$_2$ adsorption on the metal surfaces.
These studies emphasize the power from combining BE, vibrational frequency, APXPS with QM for discovering the fundamentals underlying CO2 reduction. These unexpected findings will stimulate new thinking about the CO2 reduction. These unexpected findings will stimulate new thinking about the CO2 reduction. These unexpected findings will stimulate new thinking about the CO2 reduction. These unexpected findings will stimulate new thinking about the CO2 reduction. These unexpected findings will stimulate new thinking about the CO2 reduction. These unexpected findings will stimulate new thinking about the CO2 reduction. These unexpected findings will stimulate new thinking about the CO2 reduction. These unexpected findings will stimulate new thinking about the CO2 reduction. These unexpected findings will stimulate new thinking about the CO2 reduction. These unexpected findings will stimulate new thinking about the CO2 reduction. 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In-situ ambient pressure X-ray photoelectron spectroscopy measurements

Ambient pressure XPS measurements were performed at Beamline 9.3.2 of the Advanced Light Source, Lawrence Berkeley National Laboratory. The beamline has a load lock chamber with base pressure of ~1 × 10⁻⁸ Torr for sample loading; a preparation chamber with base pressure of ~1 × 10⁻⁹ Torr for sample preparation, and a main chamber for sample characterization under ambient pressure condition. The beamline provides beams with a photon energy range of 200–800 eV.

The pristine Ag surface was in-situ prepared in the vacuum chamber by repeated argon sputtering (2 keV, 60 min) and vacuum annealing (900 K, 60 min), leading to a clean surface with no detectable carbon- and oxygen-based contamination. The oxygen covered Ag surfaces were prepared by annealing the samples at 430 K for 20 min, and 0.06 Torr 0₂ for 15 min, respectively.

During the APXPS measurements performed at 298 K, CO₂ partial pressure was kept at 0.3 Torr for CO₂ adsorption, whereas the total pressure was kept at 0.45 Torr with 0.3 Torr CO₂ and 0.15 Torr H₂O. The purity of the dosing gases (CO₂, H₂O) were in-situ monitored by a conventional quadrupole mass spectrometer to ensure no additional gas cross-contamination (especially, the CO and H₂ gases). The XPS spectra were collected at an incident photon energy of 670 eV, in the following order: a low-resolution survey with a binding energy of 600 eV to –10 eV, then high-resolution scans of O 1 s, C 1 s and valence band. The inelastic mean free path (IMFP) for the photoelectrons was below 0.9 nm for all the spectra collected. For each condition, samples were equilibrated for at least 30 mins before the measurement. By taking spectra at different sample spots and comparing spectra before and after beam illumination for 2 h, we found beam damage on the sample is negligible during the measurements.

Data availability

The data that support the findings of this study are available from the corresponding authors upon request.

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Author contributions

Y.Y., J.Y., W.A.G. III and E.J.C. designed the experiments. Y.Y., H.S., K.J.L. and E.J.C. performed the APXPS experiments. H.Y., J.O., T.C. and H.X. conducted the theoretical computations. Y.Y., H.Y., J.O., W.A.G. III and E.J.C. analyzed the data and wrote the manuscript. All authors contributed to the overall scientific interpretation and edited the manuscript.

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