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On the stratospheric chemistry of midlatitude wildfire smoke

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Massive Australian wildfires lofted smoke directly into the stratosphere in the austral summer of 2019/20. The smoke led to increases in optical extinction throughout the midlatitudes of the southern hemisphere that rivaled substantial volcanic perturbations. Previous studies have assumed that the smoke became coated with sulfuric acid and water and would deplete the ozone layer through heterogeneous chemistry on those surfaces, as is routinely observed following volcanic enhancements of the stratospheric sulfate layer. Here, observations of extinction and reactive nitrogen species from multiple independent satellites that sampled the smoke region are compared to one another and to model calculations. The data display a strong decrease in reactive nitrogen concentrations with increased aerosol extinction in the stratosphere, which is a known fingerprint for key heterogeneous chemistry on sulfate/H\textsubscript{2}O molecules (specifically the hydrolysis of N\textsubscript{2}O\textsubscript{5} to form HNO\textsubscript{3}). This chemical shift affects not only reactive nitrogen but also chlorine and reactive hydrogen species and is expected to cause midlatitude ozone layer depletion. Comparison of the model ozone to observations suggests that N\textsubscript{2}O\textsubscript{5} hydrolysis contributed to reduced ozone, but additional chemical and/or dynamical processes are also important. These findings suggest that if wildfire smoke injection into the stratosphere increases sufficiently in frequency and magnitude as the world warms due to climate change, ozone recovery under the Montreal Protocol could be impeded, at least sporadically. Modeled austral midlatitude total ozone loss was about 1% in March 2020, which is significant compared to expected ozone recovery of about 1% per decade.

Significance

Large wildfires have been observed to inject smoke into the stratosphere, raising questions about their potential to affect the stratospheric ozone layer that protects life on Earth from biologically damaging ultraviolet radiation. Multiple observations of aerosol and NO\textsubscript{2} concentrations from three independent satellite instruments are used here together with model calculations to identify decreases in stratospheric NO\textsubscript{2} concentrations following major Australian 2019 through 2020 wildfires. The data confirm that important chemistry did occur on the smoke particle surfaces. The observed behavior in NO\textsubscript{2} with increasing particle concentrations is a marker for surface chemistry that contributes to midlatitude ozone depletion. The results indicate that increasing wildfire activity in a warming world may slow the recovery of the ozone layer.


The authors declare no competing interest.

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two is called NO\textsubscript{3} here). NO and NO\textsubscript{2} exchange rapidly with one another in the daytime stratosphere depending on ozone abundances, temperatures, and photolysis rates. Therefore, the sum of both species is more robust to variability in temperature, ozone, or solar angle than either alone. NO\textsubscript{3} reductions in turn affect ClO and OH radicals, and all of these species participate in catalytic cycles that deplete ozone. Major volcanic eruptions of the past half-century have been shown to enhance midlatitude stratospheric ozone destruction (17–20). The 2015 Calbuco event resulted in observable reductions in midlatitude SH ozone concentrations in the lower stratosphere, consistent with calculations of chemical depletion (21). The 2020 Australian fires were associated with similar SH ozone reductions (15). The smoke’s radiative properties also locally warmed the lower stratosphere by up to a few degrees (15, 22).

A detailed model study of the 2020 Australian wildfire particles assumed that the particles became coated with sulfuric acid (22) and hence displayed similar midlatitude chemistry to background and volcanic stratospheric aerosols (Materials and Methods). That work estimated that heterogeneous reactions involving wildfire-enhanced aerosols could reduce SH midlatitude stratospheric ozone by about 5 to 10 Dobson Units (DU) from July to August of 2020. However, some studies have argued that wildfire smoke might form glassy surfaces (6) in the lowermost stratosphere, which would likely display quite different chemical reactivity from liquids. Tropospheric studies have shown that wildfire particles contain differing mixes of soot, primary organics, and secondary organic compounds as well as mineral and salts (23), dependent on such factors as the type of fuel (rainforest, woodland, etc.) and state of the fire (smoldering, flaming, etc.). While some studies have suggested somewhat-reduced uptake of N\textsubscript{2}O\textsubscript{5} when aerosols are coated with organics (e.g., refs. 24, 25), other work indicates differing behavior depending upon specific composition and such factors as whether the organic coatings are straight chain or branched (e.g., ref. 26). Therefore, observations and modeling studies that can improve the understanding of the impacts of wildfire smoke on stratospheric composition and chemistry are needed and are the goal of this paper.

We use satellite observations of NO\textsubscript{x} species and aerosols together with model simulations (from ref. 22) to examine the role of the 2020 Australian wildfire smoke in midlatitude stratospheric NO\textsubscript{x} chemistry. The abundance of stratospheric NO\textsubscript{x} has long been known to be a key marker for midlatitude heterogeneous chemistry on liquid sulfate aerosols, particularly when aerosols are enhanced (e.g., in major volcanic eruptions) (17, 27) as described in Results. We demonstrate that the satellite NO\textsubscript{x} observations provide strong evidence that stratospheric wildfire smoke drives important chemistry that can be expected to contribute to ozone depletion as long as stratospheric chlorine abundances remain elevated.

Results

We make use of three satellite records to examine the behavior of stratospheric reactive nitrogen after the Australian fires [i.e., NO\textsubscript{2} data from the Optical Spectrograph and InfraRed Imager System (OSIRIS) (28), the Stratospheric Aerosol and Gases Experiment on the International Space Station (SAGEIII/ISS) (29), and the Atmospheric Chemistry Experiment (ACE) (30)]. We also present ~750-nm extinction ratio data from both OSIRIS and SAGE III as well as from the Ozone Mapping and Profiler Suite Limb Profiler (OMPS/LP) from (31, 32). SAGE III/ISS and OSIRIS both employ absorption for NO\textsubscript{2} measurement at visible wavelengths, while ACE uses Fourier transform infrared spectroscopy. All three make use of limb-viewing geometry, either through direct solar occultation (SAGE III/ISS and ACE) or limb scattering (OSIRIS).

Fig. 1 presents monthly averaged stratospheric aerosol extinction ratio time series from the three instruments, demonstrating broad consistency between the datasets. The observations display a large perturbation to SH midlatitude aerosol extinction ratio due to the 2020 Australian fires. As noted in previous studies using OMPS (3), the midlatitude aerosol extinction ratio perturbation from the fires was shown to be in broad agreement with that following the substantial eruption of Mount Calbuco in 2015; the OSIRIS and SAGE data shown in Fig. 1 provide independent support for this conclusion. The eruption of the Ulawun volcano in the tropics in 2019 affected the aerosol loading in the tropics shortly before the 2020 fires in all three datasets. While coverage in OSIRIS and SAGE III/ISS is more limited due to their limb-viewing geometries, the three instruments nonetheless suggest similar timing and spread of the 2020 wildfire smoke. SI Appendix, Fig. S1 presents the extinction ratios at 675 nm as estimated by the model in ref. 22 and shows good general agreement with OMPS despite the small difference in the wavelengths available for each. Smoke particles accumulate water, increasing extinction and providing added surface area to drive faster heterogeneous chemistry, just as added sulfate does following volcanic eruptions, but with different hygroscopicity (Materials and Methods).

Fig. 2 displays the corresponding monthly averaged satellite NO\textsubscript{x} anomalies obtained from the OSIRIS and SAGE III/ISS NO\textsubscript{2} data at 18.5 km (Materials and Methods) along with the NO\textsubscript{2} change calculated in the model. OSIRIS data indicate that 2020 NO\textsubscript{2} was lower than all previous years since 2002 throughout a broad range of latitude for multiple months, from 30 to 60°S (Fig. 2), so this region was selected for focused study in this paper. OSIRIS data display larger variability at lower latitudes (particularly below about 19 km), making identification of wildfire impacts challenging equatorward of about 30°S. Furthermore, Ulawun may have perturbed tropical NO\textsubscript{2}, but the abrupt NO\textsubscript{2} change in early 2020 (at least for latitudes poleward of 30°S) suggests that the fires dominated at these latitudes. SAGE III/ISS NO\textsubscript{2} data show very similar timing and spread of the midlatitude anomaly to OSIRIS, although with more limited coverage. ACE NO\textsubscript{2} data also have limited coverage and are shown in SI Appendix, Fig. S2; these are not converted to NO\textsubscript{x} here because the fire data collection limitations following the AUOC measures both NO and NO\textsubscript{2} directly, but the NO retrieval is still under development. Nonetheless, ACE NO\textsubscript{2} data display consistent features to the other datasets. Observed 2020 anomalies in reactive nitrogen species at 18.5 km from 30 to 60°S relative to other available years are at least 20% or larger in all three satellite datasets, a large change. Magnitudes of the NO\textsubscript{x} perturbations from OSIRIS and SAGE data are different in part because of differences in coverage as well as the number of available sunrise versus sunset data points in each. Fig. 2 also shows the spread of the ensemble mean NO\textsubscript{x} change at 18.5 km calculated in the model, defined as the difference between the smoke versus no-smoke runs, and the model is in good general agreement with the data. Note that the model calculations shown here did not include the Ulawun eruption and thus reflect purely the calculated NO\textsubscript{x} change from smoke particle chemistry. A latitude height plot for March comparing the model and OSIRIS data are presented in SI Appendix, Fig. S3, again showing broad consistency between the model and the data. The 18.5-km altitude was selected for focus in this paper in order to balance OSIRIS data quality (better at higher rather than lower altitudes) and levels displaying extensive SH NO\textsubscript{x} perturbations as shown in Fig. 2 and SI Appendix, Fig. S3.

While dynamical contributions to the anomalies cannot be ruled out, Fig. 3, Top probes this region in more detail and shows that for February and March monthly averages at 18.5 km, the OSIRIS NO\textsubscript{x} amounts are lower than observed in any previous year of the available 20-y record, strongly suggestive
that the wildfires drove the change. ACE data presented in SI Appendix, Fig. S4 also display record lows for March and April 2020 in a record spanning 17 y. The chemical mechanism responsible is discussed further below. The OSIRIS data also indicate a large influence of the Calbuco aerosols on NOx, beginning in the latter half of 2015 and extending into 2016. Indeed, while 2020 OSIRIS data show the lowest NOx observed in this region in February and March, the second lowest is 2016 after Calbuco. By August 2020, the wildfire smoke impact on NOx appears to have diminished in the OSIRIS observations, and concentrations in the latter half of the year are within the range of other years. Fig. 3, Bottom presents the calculated NOx concentrations from 20 realizations in the model for the smoke and no-smoke cases. The OSIRIS observations for March indicate about $1 \times 10^9$ molec/cm$^3$ after the fires versus about $1.4 \times 10^9$ in other years, and the model results are very close to these values.

The primary chemical mechanism driving NOx reductions with increasing stratospheric sulfate aerosols and its implications for midlatitude ozone losses have long been known (16, 17, 33). Even for background aerosols, these processes decrease midlatitude ozone column abundances by several percent compared with estimates using only gas-phase chemistry for current levels of stratospheric chlorine loading. As chlorine abundances diminish in the future because of the phaseout of chlorofluorocarbons under the Montreal Protocol, the ozone depletion can be expected to decrease and eventually flip sign to positive values (34), but depletion can be expected through the mid-21st century. Further, these reactions were responsible for enhanced midlatitude ozone destruction following several past volcanic eruptions (e.g., El Chichon and Pinatubo) (19, 20).

The principal lower stratospheric photochemical mechanism is well established: NO is converted entirely to NO2 at night, which goes on to form NO3 and then to N2O5. The NO3 intermediate photolyzes rapidly in daytime, so the formation of N2O5 is only rapid at night. Hence, N2O5 is an important nighttime reservoir for NOx. A critical reaction under warm midlatitude conditions is the heterogeneous hydrolysis of N2O5, which converts reactive nitrogen to HNO3—a process that does not occur in the gas phase. N2O5 photolyzes fairly rapidly during the day.
while HNO3 photolysis is much slower in the lower stratosphere (order of a week or more). Nighttime conversion of N2O5 to HNO3, therefore, reduces NOx, which in turn means that the NO2 concentration available to form ClONO2 is reduced, leading to an increase in ozone-destroying ClO. Reductions in NOx influence HOx radicals as well (19, 35), which are also important for ozone-loss chemistry. N2O5 hydrolysis on sulfuric acid/water particles has been extensively studied in the laboratory and occurs with high efficiency (36) at essentially all atmospheric temperatures. More-recent studies have shown that BrONO2 hydrolysis is also important for heterogeneous HNO3 formation under these conditions (37), while CIONO2 hydrolysis contributes at colder conditions (i.e., temperatures below about 195K) (33). Here, we use satellite observations to probe whether similar composition changes occur due to wildfire smoke. Because HNO3 concentrations are much larger than those of NOx at the altitude range considered, NOx is a better indicator of this chemistry than HNO3 would be. Observations also indicate that some HNO3 was taken up by these particles (38), perhaps due to their high organic content (39).

A key point first made by ref. 17 is the role of nonlinear chemistry that occurs with increasing aerosol loading. While the rate of N2O5 hydrolysis increases rapidly at lower aerosol content, the reaction saturates when HNO3 is formed fast enough to remove essentially all the N2O5 formed in a given night, due to slow release by HNO3 photolysis the following day in the lower stratosphere. Further increases in aerosols, then, cannot significantly increase the reaction rate, because N2O5 is already being destroyed as fast as it can be produced (i.e., formation of NO3 and hence N2O5 through the nighttime NO2 + O3 reaction becomes the rate-limiting step).

This heterogeneous chemistry leads to a characteristic curve of decreasing NOx abundances versus increasing aerosols (17), a diagnostic fingerprint of this chemistry. Fig. 4 presents such curves for 40 to 45°S at 18.5 km using available SAGE III/ISS sunrise and sunset NOx data, OSIRIS NOx data, and NOx calculated in the smoke model. Observations and model results are deseasonalized by month using all available years of data (Materials and Methods). High extinction values are observed without low NOx in January 2020 when the plume had freshly entered the stratosphere, suggesting that the timescale for the chemistry is of order 1 mo. The 2020 observations reveal the expected decay in agreement with the model. We note that the rate-limiting gas-phase reaction NO2+O3 →
NO$_3$ + O$_2$ is faster by about 7% due to the smoke-induced warming in the March ensemble mean (212.15 K versus 210.9 K) at 40 to 45°S and 18.5 km. This temperature change is, however, only a small contribution to the modeled NO$_x$ changes compared to the more-than-threefold March surface area change and hence increased N$_2$O$_5$ hydrolysis rate due to the smoke. The OSIRIS data suggest that the peak 2020 NO$_x$ reduction driven by the wildfires may have exceeded that from the Calbuco volcano, but it should be recalled that OSIRIS did not sample this region immediately after that eruption and did promptly sample the smoke. OSIRIS data suggest that the N$_2$O$_5$ hydrolysis reaction reached its saturation limit on the wildfire particles, a finding also suggested by the SAGEIII/ISS data albeit less clearly because of the limited coverage. The model is less clear regarding saturation but is in broad agreement with the decline. SI Appendix, Fig. S5 shows that similar behavior is observed in the ACE NO$_2$ record as well, despite limitations of coverage and differences in the wavelengths of the extinction measurements.

Fig. 4 strongly supports the view that the Australian wildfire particles drive hydrolysis of N$_2$O$_5$ in a manner that is similar to sulfate particles. Thus, the presence of organic matter along with sulfate (15) apparently did not render the particles sufficiently glassy to inhibit the uptake of water needed to allow N$_2$O$_5$ hydrolysis. Fig. 4 supports the view taken by Yu et al. (22) that the 2020 wildfire aerosols behaved like sulfate particles insofar as their midlatitude heterogeneous chemistry is concerned.

We next compare modeled and observed midlatitude ozone changes but do not consider Antarctic ozone hole behavior. Polar stratospheric clouds (PSCs) are responsible for the extreme austral springtime ozone losses found in the Antarctic through heterogeneous chlorine and bromine chemistry (40, 41) and are enhanced after volcanic eruptions (42). They are composed in part of liquid sulfuric acid, water, and nitric acid. It is plausible that the Australian smoke particles may have enhanced PSC reactions and perhaps influenced midlatitude ozone indirectly through transport of reduced ozone values from the ozone hole, but this chemistry is not examined here. The model used here did not include the wildfire aerosols in their PSC reaction set, allowing us to isolate the midlatitude chemistry alone (i.e., as distinct from any transport from the ozone hole region at polar latitudes) with high confidence.
Fig. 4. Monthly mean deseasonalized NOx versus aerosol extinction at 18.5 km and from 45° to 40°S for the model (A), OSIRIS (B), and SAGE II/ISS (C and D). The years 2015 and 2016 (after the Calbuco eruption) and 2020 and 2021 (after the Australian black summer fires) are in colors, while the other years make up the gray points. Outliers greater than four median absolute deviations from the median were removed from the OSIRIS NOx and SAGE II/ISS NOx data. Model points are averaged results for each month from each of the 20 ensemble members.

Discussion

Multiple satellite datasets for stratospheric aerosol extinction and NOx perturbations following the Australian wildfires of 2020 have been compared to one another and to recently published model calculations in this paper. Record-low NOx abundances in the SH midlatitude lower stratosphere were measured by OSIRIS and ACE. SAGE II/ISS observations only extend over about the past 3 y but also display exceptionally low NOx in 2020, comparable to the anomalies found in the other two instruments. The observed seasonal and latitudinal changes in NOx near 18.5 km are broadly consistent with modeling results. Most importantly, the satellite data from both OSIRIS and SAGE II/ISS indicate large decreases in NOx abundances, which saturate with increasing aerosol extinction values, in good agreement with the model. This characteristic behavior has been previously studied (17). Its occurrence in three sets of satellite measurements presented here strongly suggests that the wildfire aerosols drove hydrolysis of N2O5 on wet particles. Thus, the evidence indicates that this key heterogeneous reaction was indeed enhanced on the Australian fire smoke surfaces, just as it is following major volcanic eruptions (e.g., Calbuco in the SH in 2015). The impact of that volcanic eruption on NOx was also shown to be discernible in the OSIRIS data but was smaller than that obtained following the 2020 fires in the monthly averages for February and March.

Decreased NOx and NO2 related to N2O5 hydrolysis is expected to be accompanied by increases in HOx and ClO, which drive net decreases in midlatitude ozone following major volcanic eruptions (19, 20). Decreases in midlatitude SH ozone of up to 8 DU were also observed after the Australian fires, and these reductions began prior to the formation of the springtime Antarctic ozone hole, indicating a local origin rather than transport of low ozone air from the ozone hole. Model results display chemical ozone decreases from about −40 to −50°S that are similar in their evolution from March through August but smaller in magnitude (with peak values of about 15
The discrepancy may be due to dynamics or to added chemistry not represented in the model. We note that the Australian smoke was unusual in that it came largely from eucalyptus trees (3, 6), and whether similar chemistry can occur on other sources of stratospheric smoke more typical of other landscapes is not known. Laboratory work to elucidate the heterogeneous reaction rates that may occur in the stratosphere on mixed organic/sulfate particles is badly needed as well as field and ongoing satellite observations to better understand their composition and chemistry.

Overall, this work provides strong evidence that the Australian forest fires of 2020 resulted in chemical impacts on midlatitude stratospheric NO$_x$ in a manner similar to that observed following volcanic eruptions. Modeled austral midlatitude total ozone loss was about 1% in March 2020, which is significant in magnitude (albeit limited in space and time) as compared to expected ongoing SH midlatitude ozone recovery due to the Montreal Protocol of about 1% per decade (43). The results suggest that this chemistry contributed to but did not fully capture the observed ozone changes following the fires. These findings are important given the uncertainties surrounding the chemistry that may occur on and in smoke particles. Our findings are suggestive that the Australian fire smoke did behave like sulfate aerosols and might therefore also have affected liquid PSCs and the Antarctic ozone loss in 2020 as well. Further work is required to examine that important chemistry and dynamics in detail. Finally, evidence strongly suggests that wildfire frequency and spatial extent has strongly increased and will continue to increase in the future due to climate change until ecosystem changes reduce available fuels. Their composition and chemistry.

The materials and methods section discusses the details of the chemical box model used to calculate the ozone changes. NO$_2$ data are available since 2002 from the OSIRIS instrument based upon limb-scattered solar radiation, version 7.1. OSIRIS data have been compared to other measurements including the solar occultation method for NO$_2$ employed by SAGE III/ISS version 5.1 (29). Broad agreement between the SAGE III/ISS dataset and OSIRIS NO$_2$ has been demonstrated (44). The OSIRIS data for the morning orbit node are shifted to a common local solar time of 12:00 PM. SAGE III/ISS and SAGE III/ISS data are converted to NO$_x$ using the photochemical box model described in ref. 45. NO$_2$ observations are also presented in the supplement from the ACE, which employs Fourier transform infrared spectroscopy in solar occultation mode at sunrise and sunset as well (46). Total ozone data are from the OMI (47).

Monthly mean values are calculated for each of the instrument datasets for any month containing at least five measurements. High-latitude winter data are always missing in OSIRIS, SAGEIII/ISS, and ACE due to lack of sunlight for the measurement. SAGE III/ISS and ACE data are generally limited by their orbits and occultation opportunities. Other gaps indicate data dropouts, especially for the aged OSIRIS instrument. The data are deseasonalized by subtracting the overall mean value for a given month of the year from that month (i.e., the overall mean January is subtracted from each individual January). Extinction ratio data at ~750 nm are available from both OSIRIS and SAGE III as well as a third instrument, the OMP5/LP. ACE includes two imagers, which measure aerosol extinction at 525 nm and 1,020 nm. OMPS extinction data shown here use the tomographic retrieval developed at the University of Saskatchewan (32). SAGE III/ISS and OSIRIS both measure limb extinction at visible/near infrared wavelengths, providing a useful comparison to the tomographic inversion approach used with OMPS.

Observations are compared to modeling results for the 2019 through 2020 Australian fires from the Community Aerosol and Radiation Model for Atmospheres (CARMa) coupled with the Community Earth System Model (CESM-CARMa) presented in ref. 22. The model includes 56 vertical layers from the top of the atmosphere down to the surface. The models are initialized with the same atmospheric state and then allowed to evolve independently. The results show that the model captures the observed changes in ozone and NO$_2$ concentrations, but there are many uncertainties including the chemical unknowns discussed herein. This paper has highlighted the need for further examination both of the chemistry of wildfire smoke in the stratosphere and the projected recovery of the ozone layer using coupled chemistry–climate–vegetation models.
surface of the Earth to about 45 km and a resolution of about 2° in latitude and longitude. The model was spun up in specified dynamics mode nudged to the Goddard Earth Observing System version 5 analysis from midsummer to the end of 2019, after which 20 perturbed initial condition runs were carried out in free-running mode from December 29, 2019, to the end of 2020. Smoke was input from December 29 to 31, 2019, and on January 4, 2020, the dates when PyroCb were observed in the stratosphere (48).

The 20 smoke ensemble members are paired with a control run (no-smoke) in order to study the impacts of initial conditions. Several test cases were conducted to probe the sensitivity of the aerosol abundances and lofting to the amount of injected material and the percentage of black carbon in the initial smoke plume. Results are shown from the case that agreed best with observations, in which it was assumed that the amount of smoke was three times that injected by the Pacific Northwest wildfire fires and 2.5% black carbon.

Heterogeneous chemistry and extinction are enhanced in hygroscopic particles that pick up water and swell, providing increased surface areas as well as water content. Like sulfate aerosols, organics are assumed to pick up water in the model but with a lower hygroscopicity. The adopted hygroscopicity of sulfate is 0.8, while the adopted hygroscopicity of organics is 0.5 and that of black carbon is 0.1. Therefore, the smoke particle sizes are not as large as those that would occur for comparable sulfate particles. We determine the swelling of the mixed particles differently from pure sulfuric acid, based on weight percent calculation. Details are in ref. 49 (A1.4 for pure sulfuric acid and A6.2 for mixed particles). Available model calculations of extinction ratio used here are at a slightly different wavelength than the observations, 675 nm.

Data Availability. All study data are included in the article and/or SI Appendix. Previously published data were used for this work (Model output used is available at https://doi.org/10.5067/OMPS.APOLLO.9.2029).

OSIRIS data are available at https://research-groups.usask.ca/osiris/data-products.php#OSIRISLevel2DataProducts. SAGE II/III data are available at https://adsac.larc.nasa.gov/project/SAGE%20II/-III/gbsbsp.51. OMPS aerosol data are available at https://zenodo.org/record/4029555. ACE data are available through the following sign-up link: https://database.sciat.ca/zbigrnp.php. OMI ozone data were obtained from https://acd-ext.gsc.nasa.gov/anonftp/кому.

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