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# "In Vacuo" Analysis of LTX Wall Samples Exposed to Lithium and Implications for High-Z Plasma-Facing Components in NSTX-U

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**Abstract:** The application of lithium to plasma-facing components (PFCs) has long been used as a technique for wall conditioning in magnetic confinement devices to improve plasma performance. Determining the characteristics of PFCs at the time of exposure to the plasma, however, is difficult because they can only be analyzed after venting the vacuum vessel and removing them at the end of an operational period. The Materials Analysis and Particle Probe (MAPP) addresses this problem by enabling PFC samples to be exposed to plasmas, and then withdrawn into an analysis chamber without breaking vacuum. The MAPP system was used to introduce samples that matched the metallic PFCs of the Lithium Tokamak Experiment (LTX). Lithium that was subsequently evaporated onto the walls also covered the MAPP samples, which were then subject to LTX discharges. *In vacuo* extraction and analysis of the samples indicated that lithium oxide formed on the PFCs, but improved plasma performance persisted in LTX. The reduced recycling this suggests is consistent with separate surface science experiments that demonstrated deuterium retention in the presence of lithium oxide films. Since oxygen decreases the thermal stability of the deuterium in the film, the release of deuterium was observed below the lithium deuteride dissociation temperature. This may explain what occurred when lithium was applied to the surface of the NSTX Liquid Lithium Divertor (LLD). The LLD had segments with individual heaters, and the deuterium-alpha emission was clearly lower in the cooler regions. The plan for NSTX-U is to replace the graphite tiles with high-Z PFCs, and apply lithium to their surfaces with lithium evaporation. Experiments with lithium coatings on such PFCs suggest that deuterium could still be retained if lithium compounds form, but limiting their surface temperatures may be necessary.

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## I. INTRODUCTION

The value of lithium plasma-facing components (PFC) to improve plasma performance has long been appreciated. For example, lithium wall conditioning produced the largest increase in the fusion "triple product," i. e., the product of density, confinement time, and temperature, in the Tokamak Fusion Test Reactor (TFTR), as shown in Fig. 1.[1] Approaches for introducing lithium into TFTR included lithium pellet injection and laser ablation of lithium in an in-vessel crucible. The locations that served as limiters for TFTR discharges depended on the plasma radius. When the radius was varied, different PFC surfaces could be coated with lithium from the plasma in a process called "painting." The PFCs in TFTR were made of graphite, including the surfaces that served as plasma limiters. Over a decade later, lithium was evaporated onto the graphite PFCs of the National Spherical Torus Experiment (NSTX). Unlike TFTR, NSTX operated with divertor plasmas, and improvements to discharge performance were observed as well.[2]

Experiments with lithium walls have also been conducted in tokamaks with metal ("high-Z") walls. The PFCs in the Current Drive Experiment-Upgrade (CDX-U) were stainless steel, and a fully-toroidal "tray" at the bottom of the vacuum vessel was filled with liquid lithium to serve as a limiter. Lithium evaporated from the tray also coated up to 50% of the plasma-contacting area. When this occurred, the largest increase over predictions for energy confinement scaling in Ohmic tokamak plasmas was achieved.[3] The CDX-U device was modified to include a conducting shell that conforms to the plasma shape and renamed the Lithium Tokamak Experiment (LTX). The shell has a stainless steel liner that forms the LTX PFC. As in CDX-U, discharge performance was enhanced with the application of lithium wall coatings.[3]

Open questions remain, however, about the relationship between PFC characteristics and plasma performance. An example of why they are difficult to answer is presented in

Section II, where the complexities of the deuterium retention mechanism when lithium is applied to graphite PFCs are described. As a more expeditious means for determining PFC characteristics that better reflect conditions during plasma operations, a diagnostic called the Materials Analysis and Particle Probe (MAPP) was developed. A description of MAPP and its use in characterizing LTX PFCs with lithium coatings is provided in Section III. The results of surface analysis of samples exposed to lithium evaporation in LTX are also included. Conclusions and implications for lithium coatings on high-Z PFCs are presented in Section IV.

## II. CHALLENGES OF CHARACTERIZING LITHIUM APPLIED TO PLASMA FACING COMPONENTS

Explanations for the improved confinement with the application of lithium to PFCs in magnetic confinement devices appear to be straightforward. Among the simplest arguments is related to the way low-recycling walls lead to hotter edge plasmas and broader electron temperature profiles. Electron temperature gradients (ETGs) have long been associated with drift wave instabilities that could degrade energy confinement [5]. Reducing wall recycling would reduce ETGs, and thus improve plasma performance.

The choice of lithium as a PFC would then seem to be clear. The high chemical reactivity of lithium would enable retention of hydrogen from the plasma by the formation of lithium hydride. This simple picture should not hold, however, if the lithium were applied to graphite PFCs. It intercalates into the graphite, and does not have the same characteristics as lithium in its elemental form. As a result, it would not be expected to volumetrically convert to lithium deuteride as observed when a macroscopically–thick (5 mm) liquid lithium sample was exposed to a high deuterium fluence.[6]

The actual mechanism for the retention of deuterium in graphite PFCs was determined only after analysis of NSTX PFCs. X-ray photoelectron spectroscopy (XPS) measurements were performed after the removal of lithium compounds formed after exposure to air. They revealed chemical complexes involving lithium, oxygen, and carbon.[7] Quantum-classical molecular dynamics (QCMD) modeling compared surface compositions that included lithium, oxygen, and carbon with only lithium and carbon.[8]

When lithium and carbon alone were included, the percentage of bound deuterium that shared charges with lithium was even lower than the surface fraction of lithium relative to the carbon. This is consistent with what would be expected when lithium intercalates into graphite and binds with carbon. For a surface that included lithium, oxygen, and carbon, however, the percentage of deuterium that shared charges with lithium was again low. The fraction that shared charges with oxygen, however, was not only greater than the percentage of deuterium, but exceeded the fraction of oxygen in the original surface composition.

The QCMD results were thus able to account for the unexpected effectiveness of lithium coatings on graphite to retain deuterium. They demonstrated that binding deuterium in a system which includes lithium, carbon, and oxygen was much more effective for deuterium retention than lithium deuteride formation. The data that supported the modeling, however, were only obtained after the end of an entire NSTX operational period. A PFC tile had to be taken out of the vacuum vessel and treated to remove the lithium compounds that formed after prolonged exposure to air. It then had to be assumed that the exposed surface reflected PFC conditions during plasma operations. This demonstrates the value of being able to analyze PFC samples immediately after plasma exposure for reducing such uncertainties.

## III. *IN VACUO* SAMPLE EXPOSURE AND ANALYSIS WITH MATERIALS ANALYSIS AND PARTICLE PROBE

To address the need for *in vacuo* PFC analysis, i. e., without venting the vacuum vessel and removing PFCs, the MAPP was developed.[9] This system is designed to permit up to four samples to be exposed to plasmas. The samples could then be withdrawn, without breaking vacuum, into an analysis chamber equipped with several surface analysis capabilities. They include x-ray photoelectron spectroscopy (XPS), low-energy ion scattering spectroscopy (LEISS), and direct recoil spectroscopy (DRS). Because the samples are attached to heaters that can be controlled separately, they can be analyzed individually with thermal desorption spectroscopy (TDS) or temperature programmed desorption (TPD).

The MAPP diagnostic was originally constructed for use on NSTX. During the outage for the construction of the NSTX-Upgrade (NSTX-U), the MAPP was installed on LTX to study samples introduced into the plasma chamber.[10] The samples were made of materials that included stainless steel to match the conducting shell surface that constitute the LTX PFCs. Lithium evaporated onto LTX walls also covered the samples. These samples were subsequently exposed to LTX discharges, and withdrawn into analysis chamber under vacuum and analyzed using XPS.

Figure 2 shows the ratios of lithium to oxygen ($R_{Li,O}$), as determined from XPS measurements of the Li(1s) and O(1s) photoelectron peaks, as a function of exposure time to the residual gases within LTX after lithium deposition on the shell surfaces. The larger uncertainties at shorter exposure times were the result of lower statistics for the XPS data, due to the limited time over which the spectra could be performed. While the measurements were taken over different lithium evaporation experiments or trials, they all follow the same general trend. Within several hours after lithium evaporation, $R_{Li,O}$ reaches a level indicative of a surface that is primarily lithium oxide. This is consistent with earlier measurements of the oxidation of lithium when exposed to water vapor.[11]

The $R_{Li,O}$ remains essentially unchanged for nearly 100 hours under a partial pressure of water of about 2 x $10^{-9}$ torr, and then only slowly begins to decrease. A salient observation is that a lithium oxide PFC surface does not appear to have a substantial effect on LTX plasma performance. Figure 3 shows the maximum discharge current as a function of time after lithium evaporation. The segments refer to longer intervals between lithium evaporations that were closely-spaced in time. High plasma currents are achievable even when the PFCs are primarily lithium oxide, and continue to be obtained over ~1000 hours after lithium evaporation.

If plasma performance in LTX depends on lowered recycling, the results suggest that lithium oxide is able to bind hydrogen. This is supported by measurements of deuterium retention by a thin lithium film on a molybdenum (TZM) substrate.[12] In the absence of oxygen, deuterium was retained in the form of lithium deuteride after exposure to a flux of diatomic deuterium ions at room temperature. This was indicated by the appearance of a peak in the TPD spectrum that corresponded to the decomposition of lithium deuteride.

If the lithium was allowed to oxidize and subsequently exposed to the same deuterium flux, a peak appears in the TPD spectrum that is indicative of deuterium retention. At the same time, there was also no longer a peak corresponding to the decomposition of lithium deuteride. This could be analogous to what was found with graphite PFCs, where the binding of the lithium in a complex with carbon and oxygen inhibits the formation of lithium deuteride. However, the lithium-carbon-oxygen complex is able to bind deuterium. Similarly, the lithium oxide in the film on the TZM substrate inhibits the formation of lithium deuteride, but the presence of oxygen could still provide a means to bind deuterium.

## IV. CONCLUSIONS AND IMPLICATIONS FOR LITHIUM APPLIED TO HIGH-Z PLASMA-FACING COMPONENTS

Experiments in LTX and surface science laboratories at the Princeton Plasma Physics Laboratory and the University of Illinois at Urbana-Champaign have shown that complexes involving lithium and oxygen are capable of retaining hydrogenic species in high-Z as well as graphite PFCs. This is supported by measurements performed with the Liquid Lithium Divertor (LLD) in NSTX. The LLD as it was located in the lower divertor is shown in Fig. 4. The LLD surface consisted of ~150 μm-thick porous molybdenum that was plasma-sprayed on top of a 250 mm-thick stainless steel substrate. Lithium was then applied to the surface from evaporators located in the upper dome of NSTX.[13] It is thus likely that like the LTX shell surfaces, the LLD became a high-Z PFC with a lithium oxide coating.

Fast visible cameras had views of the lower NSTX divertor.[14] Fig. 5 shows visible camera images of this region through two different filters. The numbers correspond to the LLD segments in Fig. 4, which are mapped to be linear in the images. The upper image records the deuterium-alpha emission. The bright band appears curved, because it corresponds to the plasma strike point on the vertical section of the inboard divertor in Fig. 4. The lower image records the neutral lithium emission.

Each of the four toroidal LLD segments was installed with a set of heaters that could be controlled independently. Only three were operational, and they were used to heat segments 1, 2, and 4 to 220$^{o}$ C. The higher deuterium alpha emission for the three heated segments suggests the release of deuterium. The brighter neutral lithium emission is consistent with the heating of the segments, as higher sputtering is expected with increasing temperature.

The results from heating the LLD were similar to laboratory observations of deuterium retention in thin lithium films. Both experiments involved lithium oxide on a molybdenum substrate, and the deuterium alpha emission from the LLD occurred at about the same temperature the deuterium peak appeared in the TPD spectrum for the oxidized lithium film.

These results have implications for lithium conditioning when the NSTX-U PFCs are upgraded. The existing graphite tiles are to be replaced with TZM tiles, but the primary means for applying lithium to their surfaces will remain lithium evaporation. If deuterium retention does not require the formation of lithium deuteride, it may relax the need to maximize the amount of elemental lithium on most PFC surfaces in the near term to reduce recycling.

The major long-term challenge is to extend lithium coverage into the divertor strike point region. This will require a scheme to flow liquid lithium, and different options are being explored. As an intermediate step prior to the implementation of a fully-flowing liquid lithium divertor, tiles that are prefilled with candidate liquid metals are under consideration for high-Z PFCs in NSTX-U.[15] The liquid metal would be transported from the interior of the tile by a wick in contact with a prefilled reservoir. Like the Capillary Porous System (CPS)[15], the PFC surface would be textured to enable wetting.

Acknowledgements

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## Figure Captions

Fig. 1 – Discharges from TFTR with and without the application of lithium to PFCs are compared. The uppermost curve was obtained with lithium wall conditioning, which has the highest fusion "triple product." Reprinted with permission from D. K. Mansfield et al., Phys. Plasmas **3,** 1892 (1996).

Fig. 2 – Lithium to oxygen ratios obtained with XPS as a function of exposure time after lithium deposition on LTX shell surfaces. Note that units in the abscissa are in hours.

Fig. 3 – Maximum plasma current achieved in LTX as a function of time after lithium deposition on LTX shell surfaces. Note that the units in the abscissa are in days.

Fig. 4 – Interior of NSTX showing LLD segments in lower divertor region.

Fig. 5 – Filtered visible camera images showing (a) deuterium alpha ($D_\alpha$) emission and (b) atomic lithium (LiI) emission from lower NSTX divertor during plasma shot. Reprinted with permission from F. Scotti *et al.,* Rev. Sci. Instruments **83,** 10E532 (2012)

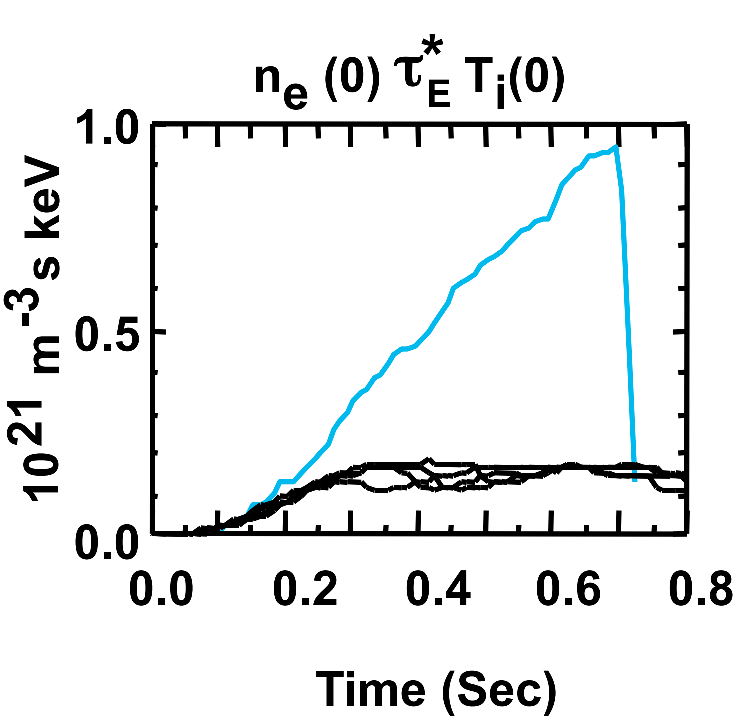
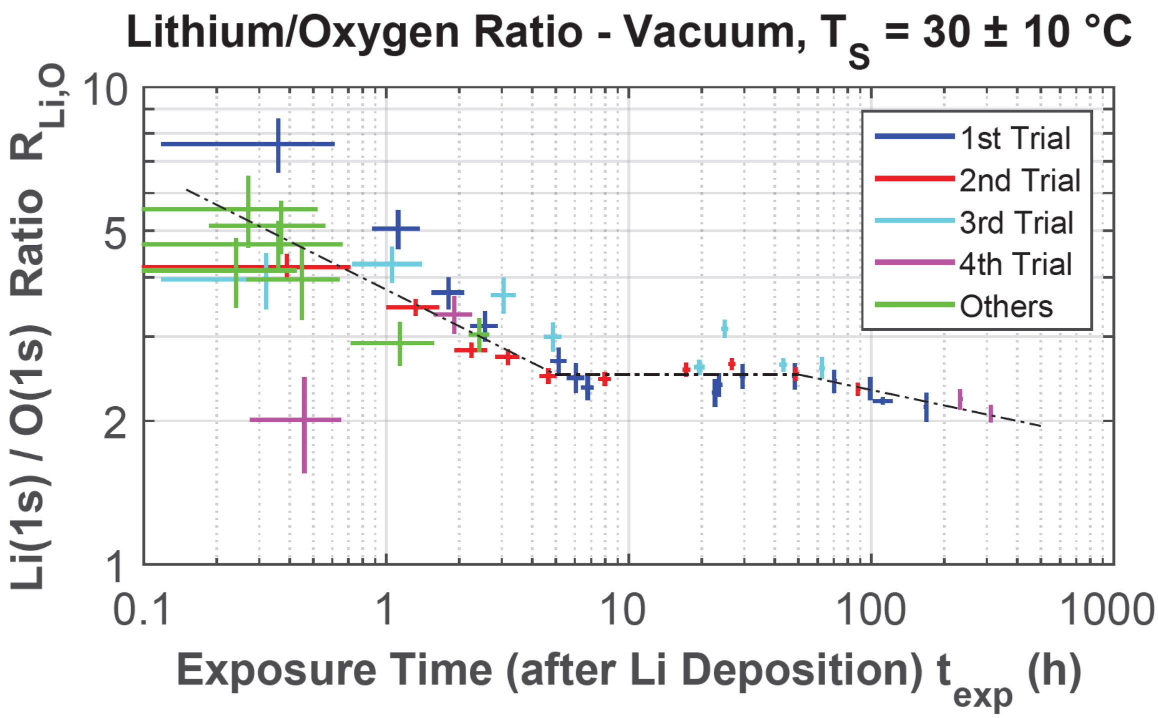



**Figure 1**



Lithium/Oxygen Ratio - Vacuum, $T_S$ = 30 ± 10 °C
Li(1s) / O(1s) Ratio $R_{Li,O}$
Exposure Time (after Li Deposition) $t_{exp}$ (h)
1st Trial
2nd Trial
3rd Trial
4th Trial
Others
10
5
2
1
0.1
1
10
100
1000


**Figure 2**

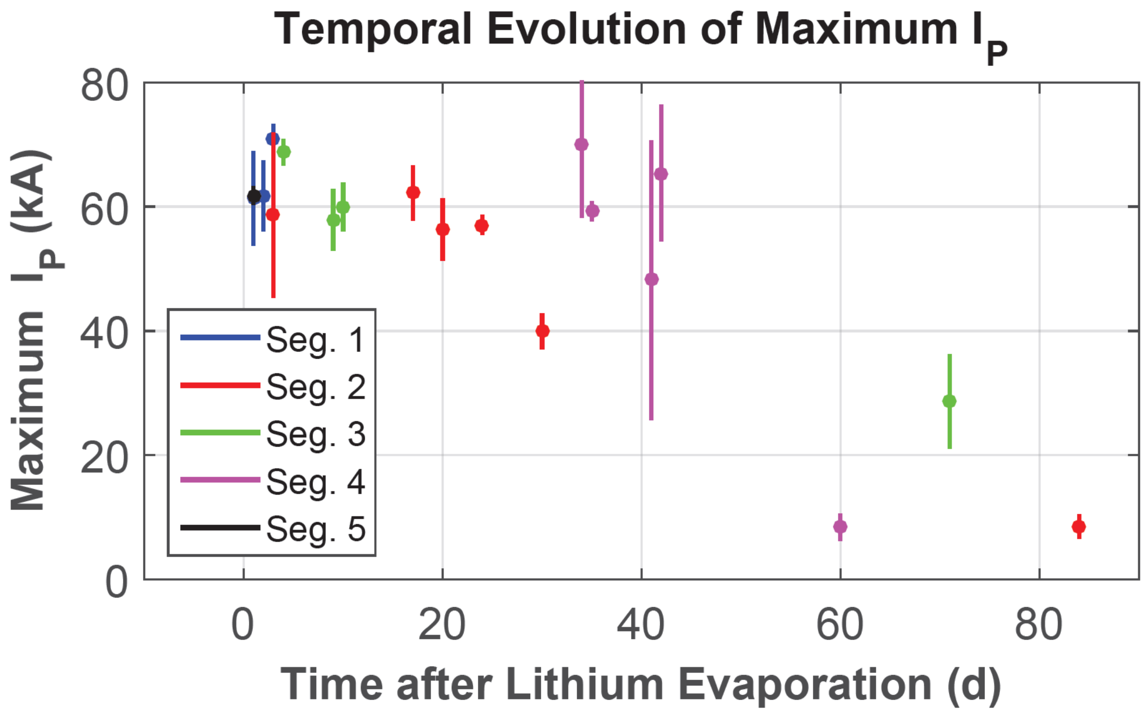

Temporal Evolution of Maximum $I_P$
80
60
40
20
0
Maximum $I_P$ (kA)
0
20
40
60
80
Time after Lithium Evaporation (d)
Seg. 1
Seg. 2
Seg. 3
Seg. 4
Seg. 5

**Fig. 3**

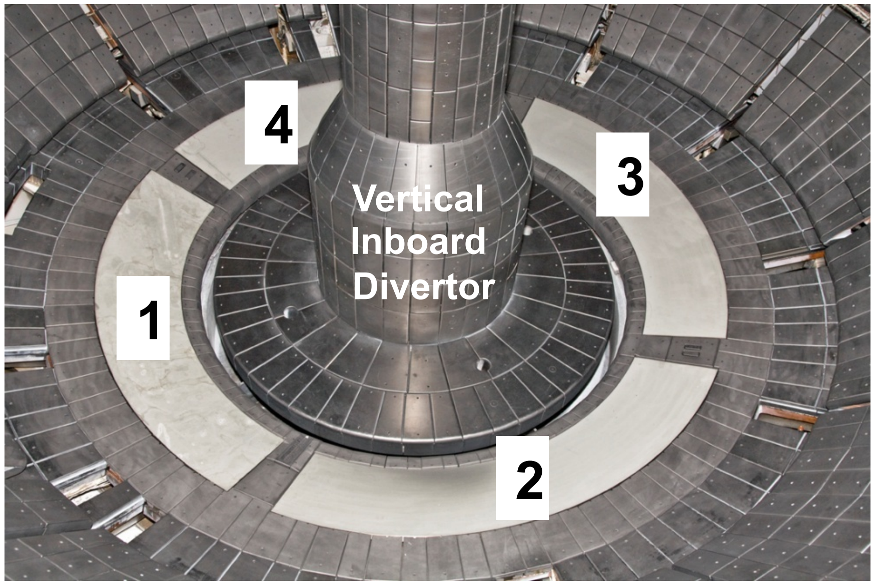
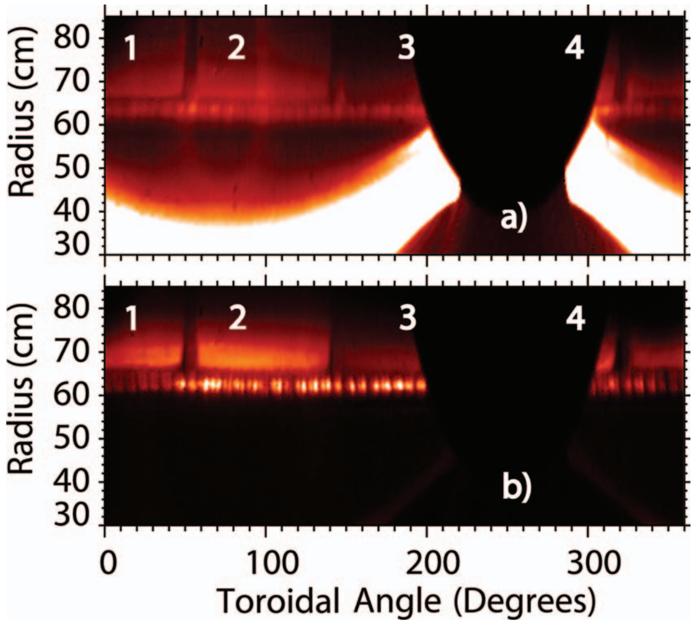



**Fig. 4**



Radius (cm)
80
70
60
50
40
30
1
2
3
4
a)
Radius (cm)
80
70
60
50
40
30
1
2
3
4
b)
0
100
200
300
Toroidal Angle (Degrees)


**Fig. 5**

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