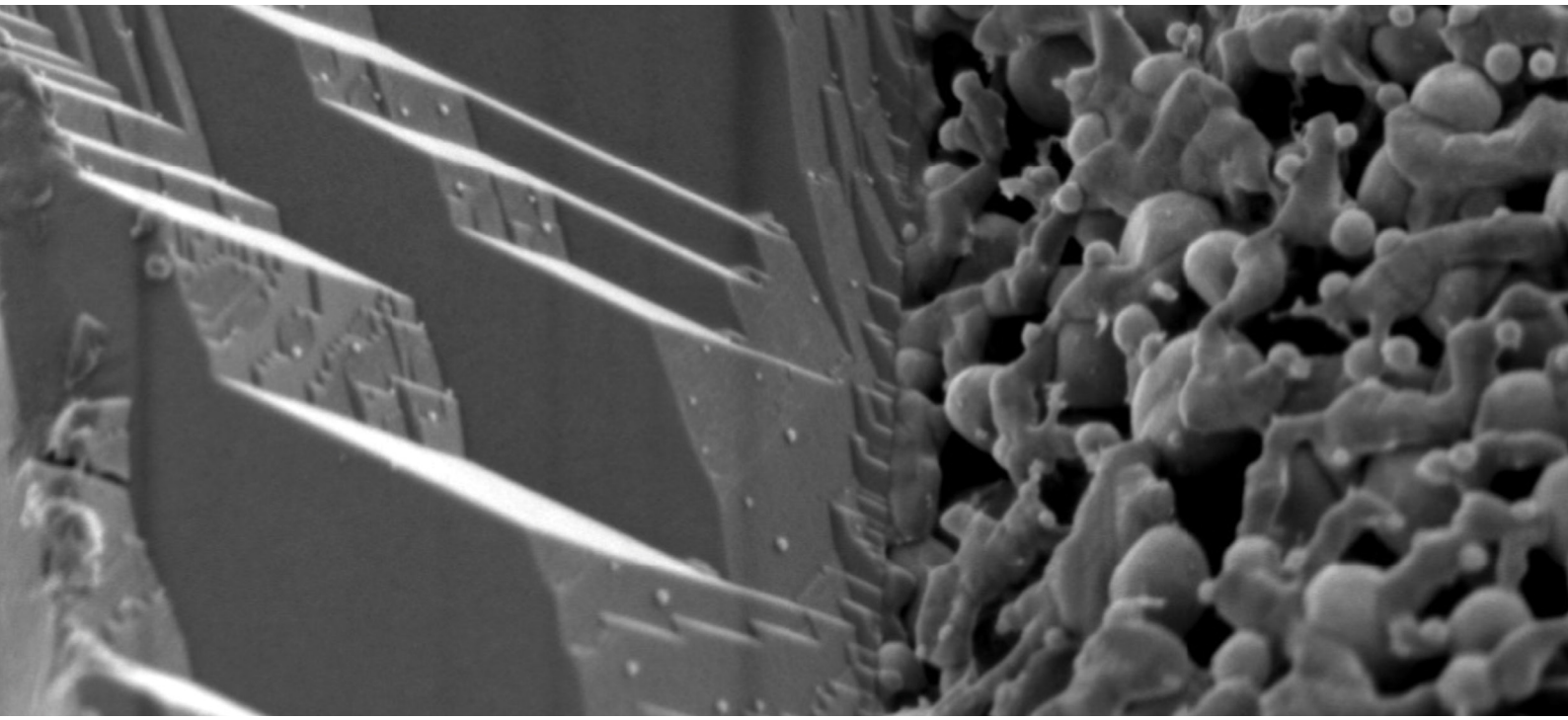
Application Note

Investigating Sweet Spot Imaging of Perovskite Catalysts Bearing Exsolved Active Nanoparticles



ZEISS

Seeing beyond

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Abstract

Platinum (Pt), generally dispersed on a solid oxide support, has been widely used for catalytic chemical reactions in automobile, chemical refining, and energy industries. During the reactions, Pt is exposed to severe conditions, e.g., high temperature events and impurities, that cause Pt agglomeration and poisoning, respectively, resulting in activity/stability losses. Perovskite materials are designed with Pt for significant catalytic properties through novel doping and exsolution methods [1].

In order to accurately determine the catalytic ability of Pt nanoparticles, it is important to understand the structure and morphology of nanoparticles. Typical scanning electron microscopy methods do not reveal the morphological characteristics of nanoparticles due to the lack of electron beam stability. Here we demonstrate imaging techniques employed to accurately determine particle size and morphology.

This method can improve the catalytic analysis of Pt loading, size, dispersion, and active sites determination.

Main

Recent advances in new energy and heterogenous catalytic materials have resulted in novel ceramics being produced for a wide array of applications such as fuel cells, autocatalysis, and chemical feedstock production [2,3,4]. One such material is non-stoichiometric A-site deficient perovskite, with a catalytically active metal doped on the B site. It is possible through controlled synthesis and reduction conditions to tailor the size and morphology of nanoparticles through emergence of the active metal cations.

To study the distribution, size, shape and morphology, careful scanning electron microscopy (SEM) needs to be deployed. The perovskite ceramic sensitivity, non-conductive nature, and nanoparticle distribution on the reduced area results in a difficult to image surface. This can often result in nano decoration being missed altogether due to lack of material understanding and microscopic technique.

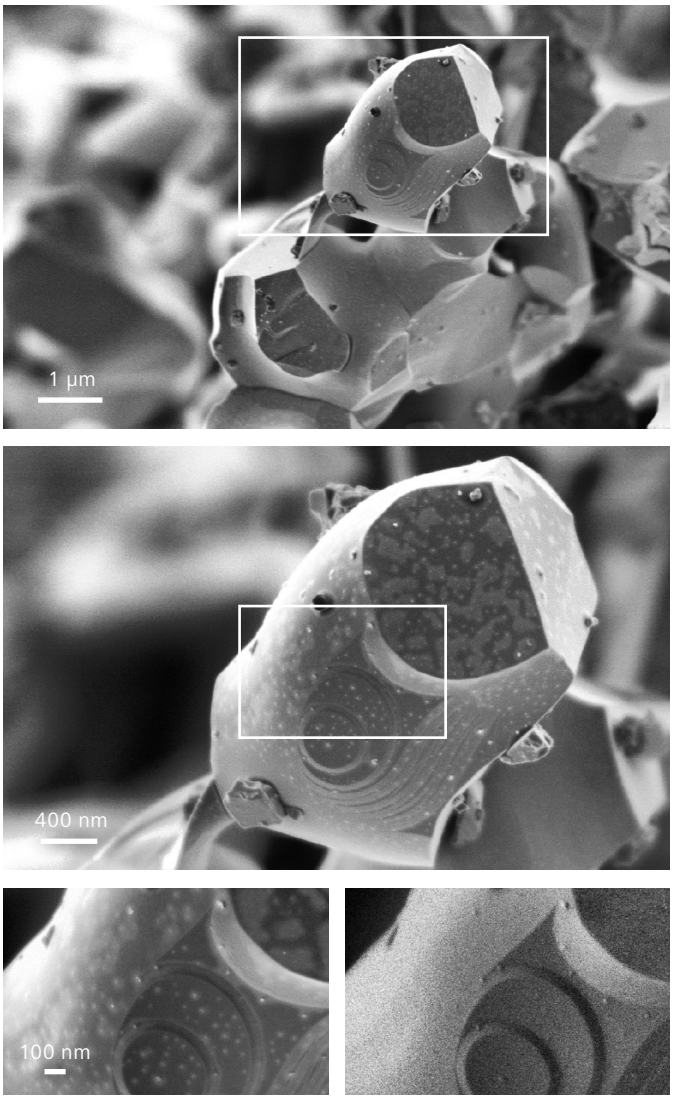


Figure 1 *Distribution of platinum decoration on reduced areas of perovskite*

Often in industrial testing for autocatalysis, a pelletized and sieved sample is observed and tested. This can lead to significant imaging issues due in part to debris, carbonaceous deposits from catalytic testing, and fine static particulate matter that can significantly reduce the sharpness of a micrograph. Typically, a solution to non-conductive materials would be sputter coat with either Gold (Au), Platinum (Pt) or Carbon (C) or a combination of coats ranging from 20 nm to 5 µm thickness for ceramic type materials. This can be counterproductive as often coating can lead to a masking of nanoparticles and false identification of both nanoparticles and carbonaceous deposits. Another factor in correctly identifying nanoparticles and distribution is the ability of substrate ceramic to be coated and catalytically react with typical desorption/adsorption-based techniques to characterize active metal sites, rendering these methods ineffective. SEM image analysis of nanoparticles is therefore a major area of interest to determine activity, stability, dispersion, and morphological features.

Electron beam sensitive materials often require additional expertise and knowledge of the SEM best practice imaging technique known as sweet spot[5] imaging. Here we demonstrate analytical micrographs of nanoparticles emerging from reduced $La_{0.4}Ca_{0.3925}Ba_{0.0075}Pt_{0.005}Ti_{0.995O3-\delta}$[1] noted as Pt+LCT.

Results and Discussion

A-site deficient perovskite Pt+LCT was synthesized using solid state synthesis and then reduced under 5% H_2/Ar resulting in 0.5 wt% Pt. Emerged nanoparticles on the surface were studied using ZEISS Sigma 300, ZEISS Sigma 500, ZEISS GeminiSEM 360 and ZEISS GeminiSEM 560. For determining imaging conditions of Pt+LCT a range of apertures, working distance from beam pole and detector choice were selected to facilitate the best imaging practice (table 1). A range of detectors available on ZEISS field emission scanning electron microsopes (FE-SEM) was chosen, all using the ZEISS Gemini electron optical column.

For ceramic type materials and non-conductive materials it is best practice to image either at low keV (<5 keV) or variable pressure with a low working distance in relation to the pole piece. This is often different for individual microscopes, especially if the detectors and beam stability are variable. To find the best practice imaging for a certain material, a sweet spot analysis is required where various parameters are run through stepwise to find the best possible imaging conditions. By running through the test matrix in Table 1 the ideal conditions for the ZEISS GeminiSEM family columns were found.

It is clear that imaging ceramics at a higher keV (above 5 keV) damages the surface and sub-surface, resulting in degradation of the material within the chamber. An area of non-interest is initially advised to be selected for use with higher keV (5-20 keV). Once an optimal keV is chosen for the solution, tailoring the working distance for advanced resolution is advised to be undertaken as the next step. Finally, an approximate aperture is required between 5 µm of the selected aperture, e.g., 10 µm-25 µm should be experimented with to find the optimal conditions and increase the brilliance of imaging. Imaging snapshots can be taken with a rapid line scan initially to acquire the appropriate imaging settings in combination with drift correction. Further image corrections can be made post scanning with the softwares ZEISS SmartSEM and ZEISS SmartSEM Touch. Once imaging conditions have been selected, it is possible to observe regions of interest without damaging the selected area.

Microscope	keV imaged	Aperture µm	SE/Inlens	VP/BSE	Ideal condition	Example
Sigma 300	10,5,3,1	50, 20, 15,10	SE & Inlens SE	VP-BSE 30 Pa	5 keV, 20 µm aperture, Inlens SE Working distance: 3.5 mm	Figure 3
Sigma 500	10,5,3,1	50, 20, 15,10	SE & Inlens SE	VP-BSE, Inlens	3 keV, 20 µm aperture, Inlens SE Working distance: 3-5 mm	Figure 4
GeminiSEM 360	10,5,3,1	50, 20, 15,10	SE & Inlens SE	VP-BSE 20-30 Pa	1-3 keV 10-20 µm aperture, Inlens SE and VP-BSE 20 Pa Working distance: 4-7 mm	Figure 5
GeminiSEM 560	10,5,3,1-<1	50, 20, 15,10	SE & Inlens SE	Inlens EsB	1-3 keV 10-20 µm aperture, Inlens SE and Inlens EsB Working distance: 2-7 mm	Figure 6

Table 1 *Range of conditions used to determine the sweet spot of the perovskite catalysts*

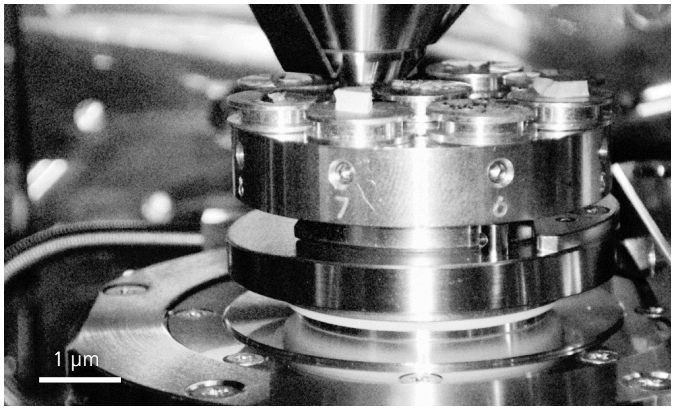


Figure 2 *Working distance (2.5 mm) needed for imaging nanoparticles on ceramic*

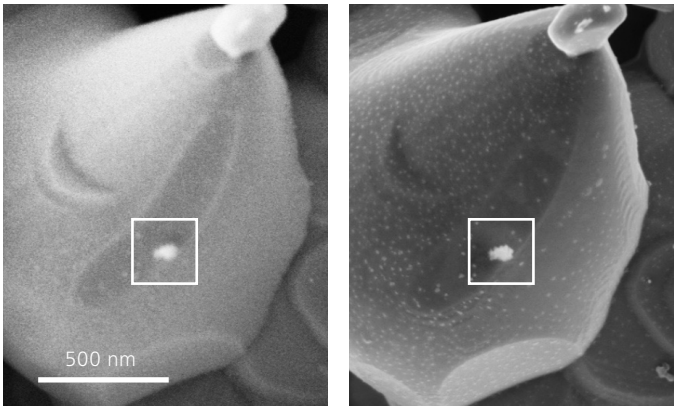


Figure 3 *(L) Standard SE detector with no decoration visible;*
(R) use of Inlens SE technology allows nanoparticle decoration to be observed

It was found that for perovskite an aperture of 20 µm was sufficient for imaging and a working distance of less than 3 mm (Figure 2) across the Sigma family was required to see nano meter scaled features on the surface of the materials.

Smaller nanoparticles of <8 nm finely dispersed on the surface of the perovskite were not completely visible with the secondary electron detector (ETSE); this can often be misleading for microscopists who can miss nanoparticle decoration by using the wrong detector. By using the Inlens SE detector, full nanoparticle decoration was visible. Images were taken using a rapid <4s line scan as any longer would result in visible beam damage to the material, as can be seen in Figure 3.

Further image correction and processing can be tailored automatically for the Sigma family. SmartSEM Touch can be used alongside imaging (Figure 4) to significantly reduce time spent correcting image sharpness as well as brightness and contrast.

For GeminiSEM 360 and GeminiSEM 560 microscopes, a magnetic-clamp Kline stage locking the eucentric stage in place was used to further stabilize the imaging as well as the pendulum-based motion stabilization for the core of the microscope. This enables a lower working distance from the pole piece and enables imaging of unstable or non-anchored particles to the stub (Figure 5).

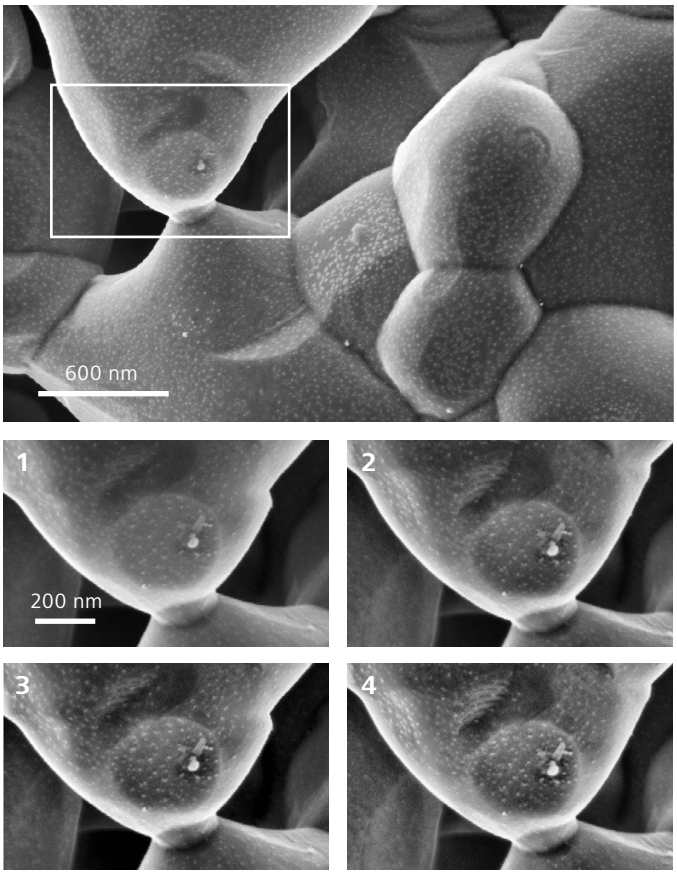
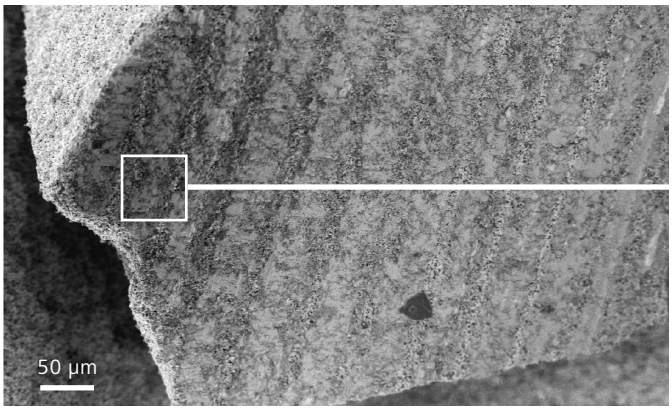


Figure 4 *SmartSEM touch allows for rapid image improvements with automated drift correction and auto brightness contrast sharpening*



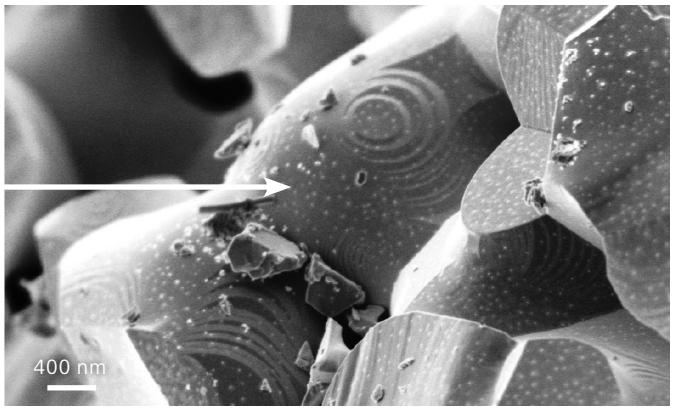


Figure 5 *Non-anchored particles can be easily observed due to the stability provided by the GeminiSEM family magnetic clamp, rendering stage movement minimal and improving image quality*

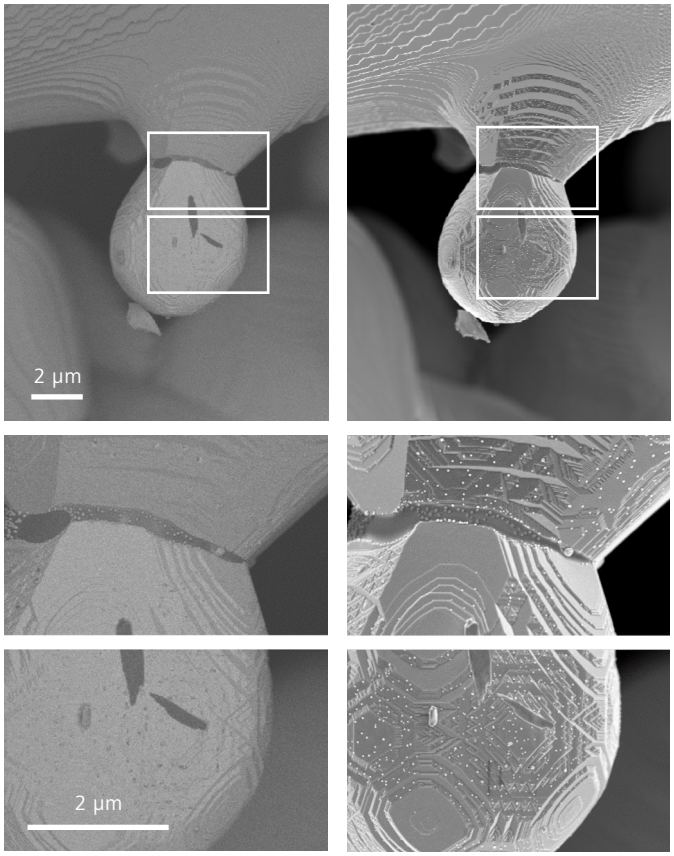


Figure 6 *Inlens BSD allows for greater contrast and sub surface morphology identification of LCCNT*

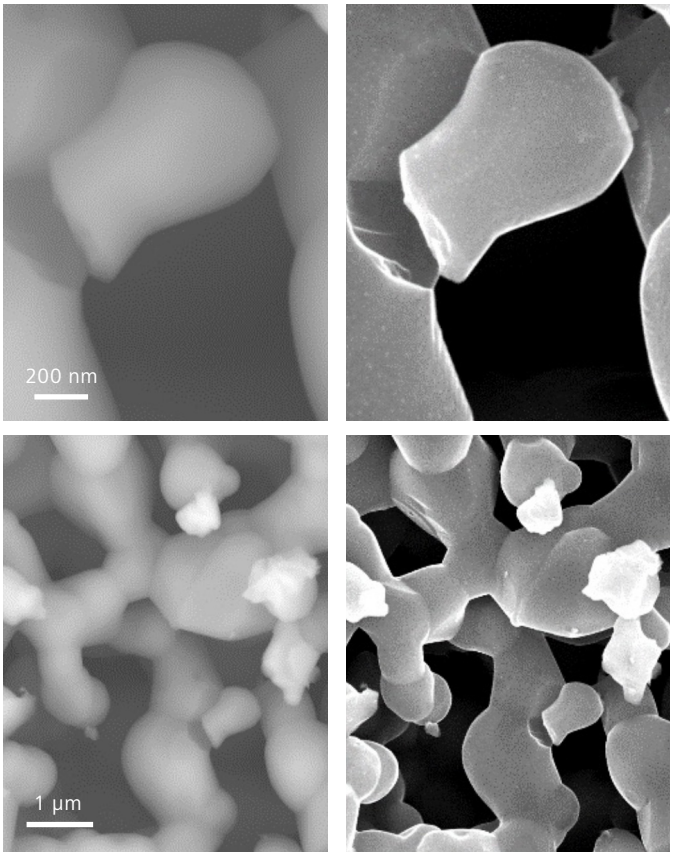


Figure 7 *The use of variable pressure mode allows for delicate imaging in both Inlens SE, SE and BSE modes with the Sigma series*

Further analytical imaging can be achieved with energy selective backscattered detector (Inlens EsB). Subsurface nanoscale composition is made visible with a clear compositional contrast. The second annular incolumn detector is located above the Inlens SE detector allows for more detailed material information and contrast in Figure 6.

Pt nanoparticles are visible in NanoVP variable pressure mode with a back scatter detector (BSD), Figure 7, and can provide structurally significant information through contrast and subsurface morphology. Further enhancement can be achieved at variable pressure alongside a low working distance relative to the pole piece (between 3-5 mm); nanoparticles are visible using VP mode. Significantly, Inlens detectors can be used in VP mode and therefore enhance imaging and provide contrast alongside BSD images.

Conclusions

Sweet spot imaging conditions can be determined for the ZEISS FE-SEM range (in this case Sigma and GeminiSEM). It plays a practical and methodical role in finding optimal conditions for imaging of samples. For ceramics such as the ones used in this study, catalytically active nanoparticles decorating an A-site deficient perovskite, careful imaging and analysis are major tools in determining catalytic activity. It was found that sweet spot imaging conditions were not dissimilar between the ZEISS Sigma and GeminiSEM families with subtle differences for each microscope type. The stability and stage of the ZEISS GeminiSEM family were found to increase image stabilization and brilliance, resulting in high resolution imaging at low keV. Alongside this, Inlens SE technology was found to be the most important in observing nanoparticle decoration for both Sigma and GeminiSEM. Further detectors can be used in parallel such as Inlens EsB to provide more subsurface and morphologically distinct regions of interest.

References

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