ISSN: 2754-4915

Journal of Material Sciences & Manufacturing Research

Research Article

Open Access

Pearlitic Morphologies Found in Carbon Steel Artefacts More than 2,000 Years Old

Laura García[1]*, A Javier Criado[2], Growene W Queirós[3], J Víctor Meseguer-Sánchez[4], José M Gómez de Salazar[1] and Antonio J Criado[1]

[1]Department of Materials and Chemicals Engineering. Faculty of Chemistry, Complutense University of Madrid, Spain (U.C.M.)

[2]GRIAL Investigation Group. International University of La Rioja, Logroño, La Rioja, Spain

[3]Rovuma University, Nampula, Mozambique

[4]Chair Agringenia-Nutripeople, Circular Economy and RSD of the UCAM" UCAM University, Murcia, Spain

ABSTRACT

The results of this research reveal the possibility of observing another type of pearlite. Formed in archaeological steel pieces a few years old. Perlite resulting from diffusion over time at room temperature. For this we show the metallographic structure of archaeological samples that have remained buried in the soils of Roman Baetica for 2,000 years. Diffusion does not stop at a given moment but takes place, undoing structures that seemed to be stable; this diffusion produces new equilibrium structures that we cannot evaluate due to lack of time. The research was carried out as part of the Archaeological Analogues project for the Spanish National Nuclear Waste Company (ENRESA), revealing the alternation of structures of hot-worked and normalized carbon steels. The microscopy used is Scanning Electron Microscopy (SEM). The specimens, among many, two were selected because they have a good corrosion-free metallic core.

Corresponding authors

Laura García, Department of Materials and Chemicals Engineering, Faculty of Chemistry, Complutense University of Madrid, Spain (U.C.M.). Email: gslaura@quim.ucm.es

Received: November 07, 2022; **Accepted:** November 14, 2022; **Published:** November 21, 2022

Keywords: Perlite, Steels, Archaeometallurgy, Metallography, Diffusion

Introduction

Professor H.D.K.H. Bhadeshia published on his Cambridge University website the term Old Pearlite, coining a new pearlitic morphology from the pearlitic morphologies published in the 2006 Journal of Nuclear Materials [1,2].

The article under review is a consequence of the publication of results obtained in a research carried out for ENRESA (Empresa Nacional de Residuos Nucleares) in Spain in the 1990s on natural analogues and archaeological analogues for the deep burial of high-level nuclear waste. The model selected by ENRESA for Spain was carbon steel containers, as in the United States and other European Union countries. This research team proposed that for the durability of the containers information could be sought in the archaeological analogues, numerous pieces that have been exposed in the most diverse soils and beds with real and not simulated chemical characteristics.

We set about the task of studying different archaeological site contexts and studying the artefacts found in relation to soil characteristics and geochemical conditions. The result was a large collection of data on corrosion and microstructural transformations suffered by these artefacts due to the natural geochemistry and, very diverse, of the different soils. In this research we were able to verify that the microstructure of the steels changed over long periods of time under natural conditions, in addition to other issues [3-4].
The dissemination of data and possible applications of research on archaeological materials resulted in various publications [5-6].

Thus it was possible to observe the microstructural changes that occur in carbon steels, the infinite majority of steel artefacts of antiquity, with the passage of time over periods of hundreds of thousands of years at ambient temperatures. And, in this way, Old Pearlite was discovered.

There are numerous scientific publications that directly address the formation of perlite morphology in carbon steels. Among other publications are those of Professor Bhadeshia, Pandit, Pearson and Verhoeven, as well as the chapter on perlite in Bhadeshia's recent book "Theory of transformations in steel" [7-13].

Professor A.J. Criado also talks about Old Pearlite, in a publication showing metallographic images obtained by scanning electron microscopy (SEM) at the National Electron Microscopy Centre of the Complutense University of Madrid (UCM) [14].

Experimental Technique

The archaeological samples for this research were selected from hundreds of archaeological pieces from different archaeological sites in the Iberian Peninsula. The selection criterion was that they retained a metallic core, although corrosion layers are abundant in some cases.

The archaeological sites that were the subject of this study were:
A: Piece of nail found in a wall of the High Imperial Roman cistern, dated to the 1st century BC transition to the 1st century AD, located in the Republican and High Imperial archaeological site of Cerro Muriano (Córdoba, Spain).

B: Nail found in a Roman tomb at the site of the High Imperial Roman necropolis in the northern part of the city of Córdoba (Spain), dated to the 1st century AD.

The samples were embedded in epoxy resin and roughened with different grit papers, from 180 to 2000. Subsequently, they were first polished with water in 0.3 µm Micropolish II alumina and finally with 0.05 µm Micropolish II alumina, both from Buehler. Finally, after cleaning with distilled water, they were attacked with 2% Nital and 5% Nital.

For their metallographic observation, they were sputtered with gold and observed metallographically under a scanning electron microscope JSM 6400 is particularly suitable for observing the surface of materials (geological, chemical-physical...) and biological, with the possibility of carrying out semi-quantitative analyses to obtain an approximation of the composition of the materials. Using backscattered electrons, it is possible to obtain the distribution of elements and phases in the study of materials.

Results

Figure 1 shows one of the external walls in steps of the Roman cistern, where the piece of nail under study was found embedded, as can be seen in Figure 2. Figure 3 shows a macrograph of the nail, prepared metallographically, showing the preserved part of the iron core.

Figure 1: Macrograph showing one of the external stepped walls of the Roman cistern where the nail under study was found

Figure 2: Macrograph showing the nail found embedded in the external wall of the Roman cistern

Figure 3: Macrograph of the nail under study, embedded and metallographically prepared, showing the iron core of the nail

Figure 4 shows a macrograph of an idealised model of the Baetica Cortuba (colonia Patricia, in Latin), oriented from North to South, where we can locate the necropolis, outside the perimeter of the city where the cremation tomb was located, next to the remains of a road (Figure 5). This was the custom of the Romans, to bury in tombs next to roads and paths

Figure 4: Macrography of an idealised model of the Betic Cortuba, oriented from north to south

Figure 5: Macrography where the cremation tomb was located, next to the remains of a causeway

Figure 6 shows the nail found in the Roman tomb, examined in a good state of preservation. Once it was cut and prepared metallographically, the good state of preservation was observed, as well as the very heterogeneous microstructure of metallic grains, as it corresponds to a steel of that time (Figure 7).

Figure 6: Macrograph of the nail from site B examined, showing its good state of preservation

Figure 7: Macrograph of the examined, deep-drawn and metallographically prepared nail in Figure 6, with a clear metallic core, with a very heterogeneous microstructure of metallic grains

The microstructure of a steel of this type but manufactured today can be seen in Figure 8; it shows a very regular structure of a pearlitic structure of a steel that has been hot-rolled and normalised. Figures 9 to 11 show the typical pearlite structure, known as Old Pearlite, of a steel of similar composition, belonging to the nail in Figure 3, and subjected to thermo-mechanical treatment under the same conditions but aged for 2.000 years. The differences are visible to the naked eye.

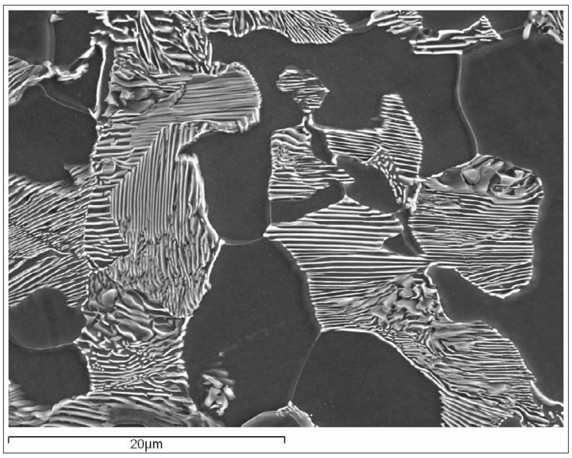

Figure 8: Micrograph, obtained by scanning electron microscopy, showing a very regular microstructure of a pearlitic structure of a steel that has been hot-rolled and normalised

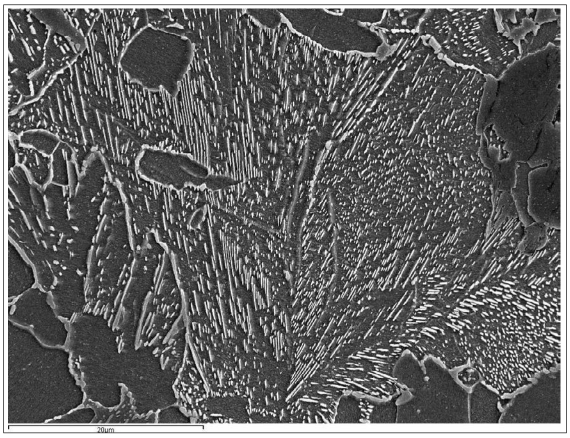

Figure 9: Micrograph, obtained by scanning electron microscopy, showing the typical pearlite structure known as Old Pearlite, of a steel of similar composition, belonging to the nail in Figure 3, and subjected to thermo-mechanical treatment under the same conditions but aged for 2.000 years

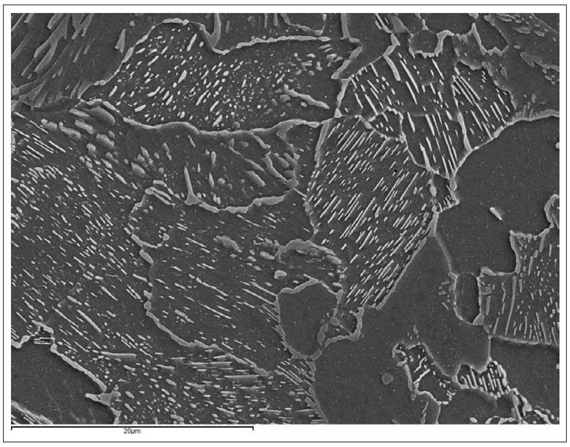

Figure 10: Micrograph, obtained by scanning electron microscopy, of the structure in figure 9, at higher magnification

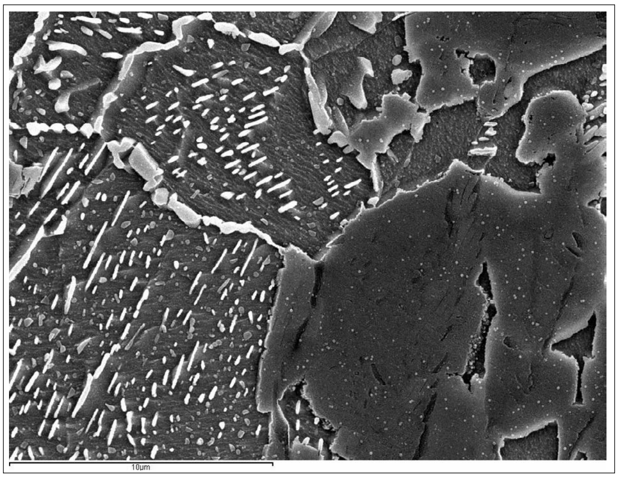

Figure 11: Micrograph, obtained by scanning electron microscopy, of the structure in figure 9, at higher magnification

In addition to a very regular structure of iron carbide crystals, a segmentation of these crystals can be observed, as well as the appearance of a cementite crust surrounding grains having the same orientation, as Widmanstätten-type structures. The large crystal observed is the result of the layer of oxides from the corrosion (Figure 15).

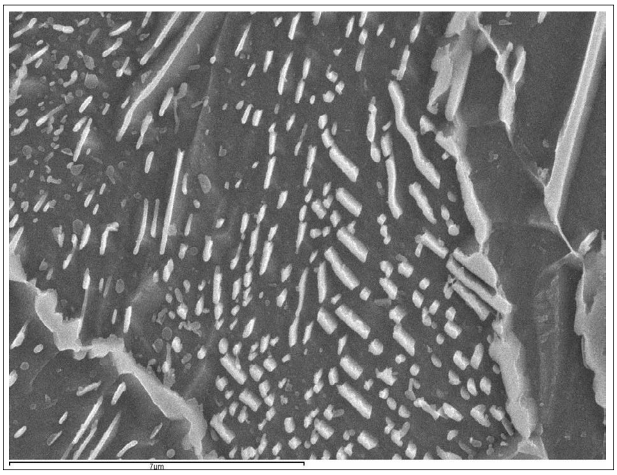

Figure 12: Micrograph, obtained by scanning electron microscopy, showing a detail of the cementite crust, practically continuous, with a very polyhedral shape of the cementite crystals

On the other hand, there is also a very evident parallelism of the structure that we have been observing in the nail in Figure 3. The pearlite laminae appear as crystals totally parallel to each other, respecting an evident directionality that seems to correspond to very well defined planes of the ferrite crystals (Figure 13).

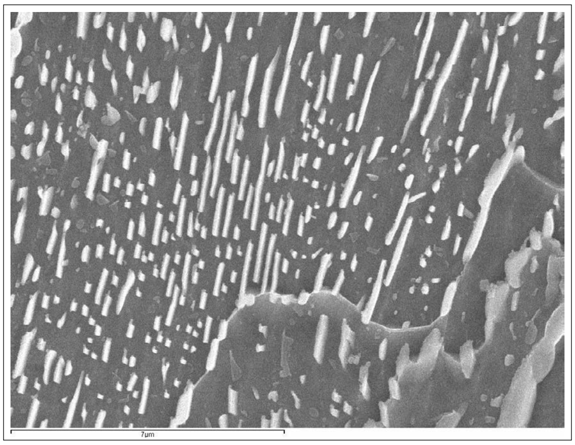

Figure 13: Micrograph, obtained by scanning electron microscopy, showing the pearlite laminae appear as crystals completely parallel to each other, respecting an evident directionality that seems to correspond to very well defined planes of the ferrite crystals

Figures 14 and 15 clearly show the Widmanstätten-type orientation of the crystals and the continuous cementite crust of the nail under study in Figure 3. The cementite crust surrounding these Old Pearlite colonies is very evident.

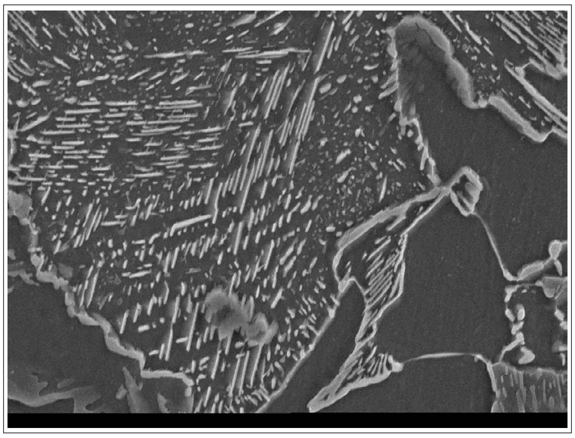

Figure 14: Micrograph, obtained by scanning electron microscopy, showing the Widmanstätten-type orientation of the crystals and the continuous cementite crust, of the nail under study in Figure 3

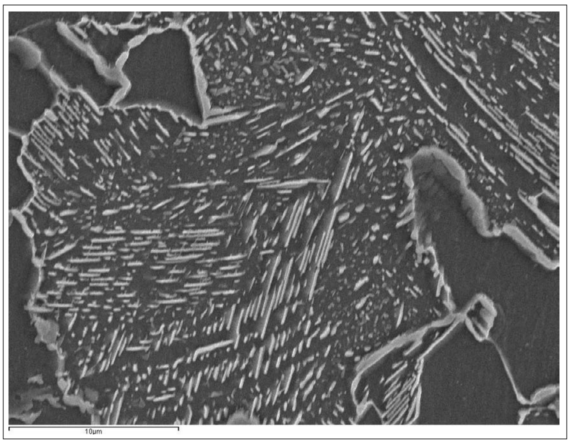

Figure 15: Scanning electron microscopy micrograph of another detail of the Widmanstätten-type orientation of the crystals and the continuous cementite crust of the nail under study in Figure 3

The 5% Nital etching clearly shows the thinness of the Old Pearlite cementite lamellae, which are bent in an evident way, to one side, showing their ductility depending on the dimensions of the laminae (Figure 16). They are probably inclined towards the movement of the liquid stream of the attack reagent. In Figure 17, this effect of the thinness of the Old Pearlite cementite laminae can be clearly seen.

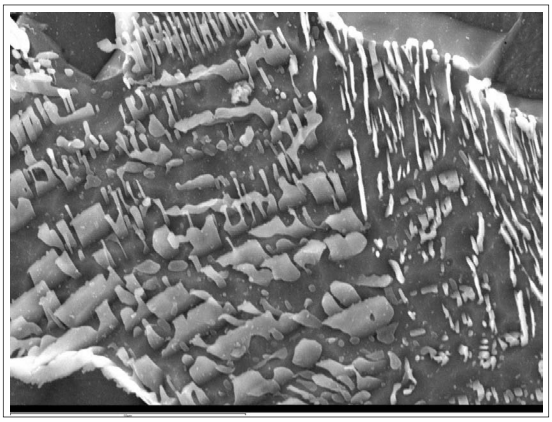

Figure 16: Micrograph, obtained by scanning electron microscopy, showing the thinness of the Old Pearlite cementite laminae, which are clearly curved to one side, showing their ductility depending on the dimensions of the laminae

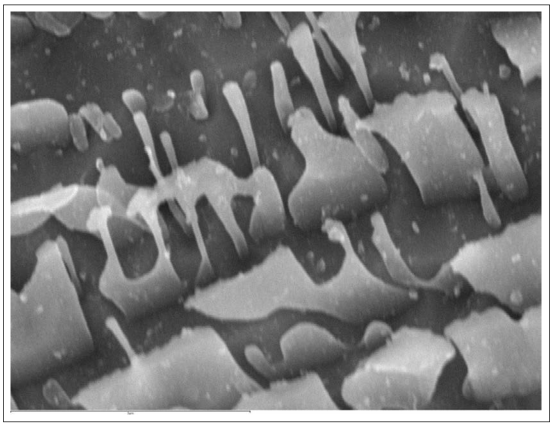

Figure 17: Micrograph, obtained by scanning electron microscopy, at higher magnifications of the previous figure

Further etching with 5% Nital shows how the cementite in the lamellae thins to extremely thin laminae (Figure 18). The grain boundary crust thickens and the flakes eventually segment into small iron carbides. This effect is best seen in Figures 19, 20 and 21; where even some of the laminae are so narrowly thin that they become detached from the matrix (Figure 20). This is a consequence of the depth of the chemical attack, some of them even becoming transparent due to their thinness. Figure 21 also shows the extreme thinness of the cementite flakes and a partial segmentation due to the thinness of the cementite laminae.

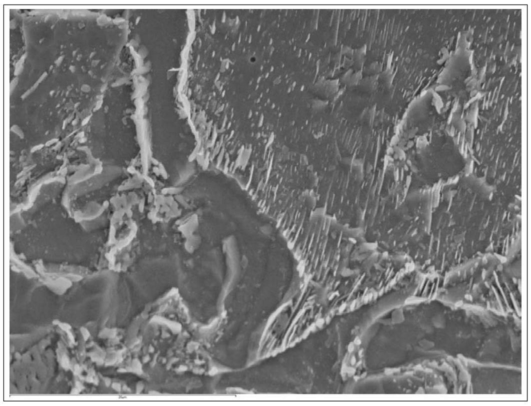

Figure 18: Micrograph, obtained by scanning electron microscopy, showing how with further chemical attack, the cementite in the laminae thins to become extremely thin

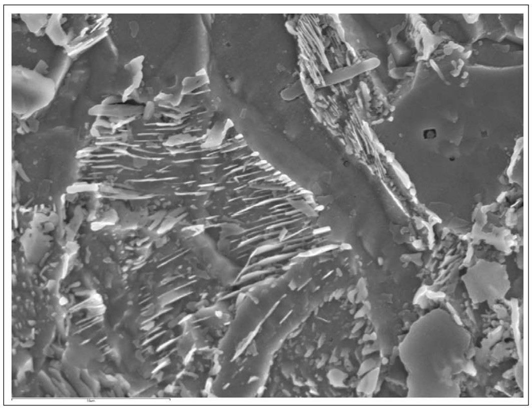

Figure 19: Micrograph, obtained by scanning electron microscopy, showing how the grain boundary crust thickens and the laminae become segmented into small iron carbides

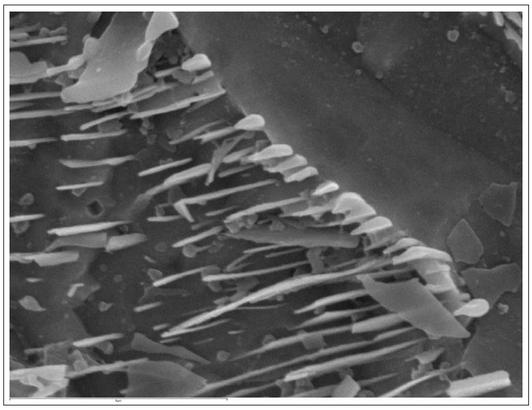

Figure 20: Micrograph, obtained by scanning electron microscopy, where it can be seen how some of the laminae, due to their dimensions, are so thin that they become detached from the matrix

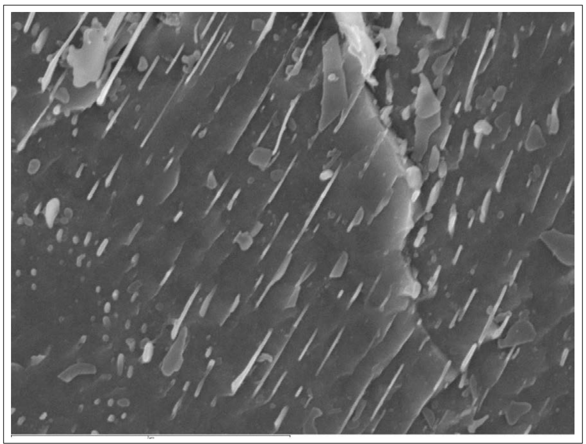

Figure 21: Micrograph, obtained by scanning electron microscopy, showing the extreme thinness of the cementite laminae and a partial segmentation due to the thinness acquired by the cementite lamellae

In the nail found in the Roman tomb, this process of segmentation of the perlite sheets is very advanced (Figures 22 and 23), which shows that the effect of time is strong with the conventional appearance of the current perlite, as shown in Figure 8.

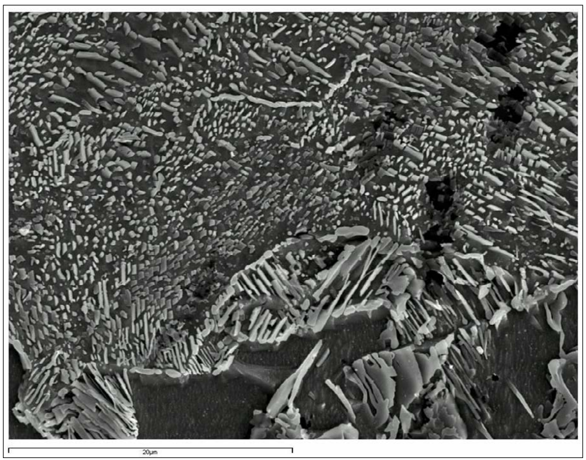

Figure 22: Micrograph, obtained by scanning electron microscopy, showing the very advanced segmentation process of the perlite laminae of the nail found in the Roman tomb

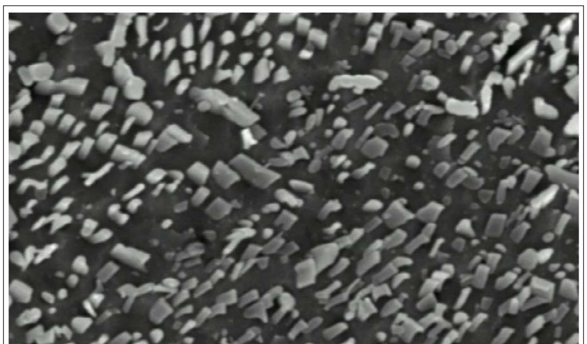

Figure 23: Micrograph, obtained by scanning electron microscopy, at higher magnifications of the previous figure

Conclusion

As we have been able to observe in the micrographs obtained from hot deformed pearlitic carbon steels cooled to room temperature, the changes in pearlitic morphology are more than evident. This means that there is a slow but effective morphological variation, over considerable periods of time, at room temperature, as is the case of these steels with more than 2000 years of very reliable chronologies.

They are a clear example of the passage of time on centuries-old archaeological metal pieces. In addition to the mechanical properties derived from the change of shape, they are a very clear vector to know the chronology of an archaeological piece.

When the shape changes, even if the chemical composition of the steel is unchanged, the variation in mechanical properties is obvious. This is of no relevance to standard parts, although it can mean an obvious change in mechanical properties.

This type of pearlitic morphology changed in shape is called Old Pearlite, to differentiate it from the morphologies of steels still unaltered by the passage of time at room temperature.

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