Technical note

Diagnosis of pathologies in ancient (seventeenth-eighteenth centuries) decorative blue-and-white ceramic tiles: Green stains in the glazes of a panel depicting Lisbon prior to the 1755 earthquake

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Decorative panels of ceramic glazed tiles comprise a valuable cultural heritage in Mediterranean countries. Their preservation requires the development of a systematic scientific approach. Exposure to an open-air environment allows for a large span of deterioration effects. Successfully overcoming these effects demands a careful identification of involved degradation processes. Among these, the development of micro-organisms and concomitant glaze surface staining is a very common effect observed in panels manufactured centuries ago. This paper describes a study on the nature of green stains appearing at the surface of blue-and-white tile glazes from a large decorative panel with more than one thousand tiles, called *Vista de Lisboa* that depicts the city before the destruction caused by the 1755 earthquake. The characterization of green-stained blue-and-white tile glazes was performed using non-destructive X-ray techniques (diffraction and fluorescence spectrometry) by directly irradiating the surface of small tile fragments, complemented by a destructive scanning electron microscopy (SEM) observation of one fragment. Despite the green staining, analytical X-ray data showed that no deterioration had occurred irrespective of the blue or white color, while complementary SEM-EDX data provided chemical evidence of microorganism colonization at the stained glaze surface.

Keywords: Tile panel, Seventeenth-eighteenth centuries, Blue-and-white glazes, Green stains, SEM-EDX, XRD, XRF-WDS

Introduction

Glazed ceramic tiles (‘azulejos’ in Portuguese, from the original Arab designation ‘al-zulayj’) have a wide application in the architectural cultural heritage of the Mediterranean area and their deterioration deserves particular attention. Churches, public buildings, or even palaces were decorated with attractive tiles, placed inside and/or outside the edifice, most of them built hundreds of years ago. Ancient tile panels exposed to different environmental conditions are liable to develop microorganisms that can play a major role in tile pathologies and materials degradation (e.g. Oliveira *et al.*, 2001; Giacomucci *et al.*, 2011).

A large panel of blue-and-white tiles, named *Vista de Lisboa,* located at the National Tile Museum (MNAz) (Mântua & Monteiro, 2010) is the focus of this study. It depicts a panoramic view of the city prior to its destruction due to the earthquake of 1755. The object has undergone successive conservation treatments (the latest in the 1990s), yet small green stains and pinkish discoloration in larger areas are perceptible in the glaze of many tiles (Castel-Branco Pereira *et al.*, 1992).

Following a previous study on environmental impacts where green stains observed in decorative blue-and-white tile panels from the sixteenth century

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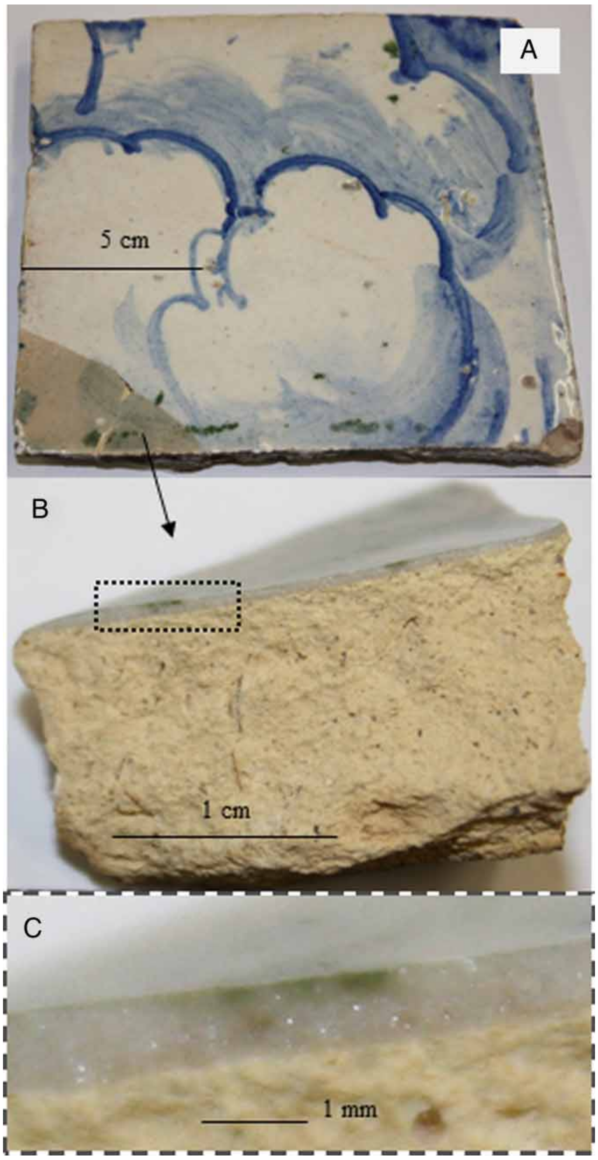

Figure 1 Studied blue-and-white tile (A) and magnified view of a fragment presenting green stains (B) plus a detail (C) showing that these stains are confined to the glaze surface.

were attributed to the presence of algae colonies (Figueiredo *et al.*, 2009), this work is focused on the tentative diagnosis of the greenish staining developed in the glaze of the *Vista de Lisboa* tile panel (Fig. 1). This study is a preliminary step toward future tile conservation involving the use of neutron beams (Dias & Prudêncio, 2007; Prudêncio *et al.*, 2012) and gamma radiation, with the purpose of removing any micro-organisms without damaging the glazed tiles.

Brief history of the tile panel Vista de Lisboa

This is one of the most remarkable blue-and-white Portuguese tile panels, both for the rarity of its iconography (Santos Simões, 1961) and for its huge dimensions (~23 × 1 m and more than 1200 ceramic tiles with dimensions of 14 × 14 cm). The iconography of the panel (churches, convents, palaces, public buildings, bridges, fountains, etc.) represents Lisbon's architecture viewed along the Tagus river border by the end of the seventeenth century. Belonging originally to a palace, the context and date of the panel manufacture are still not clear. For stylistic reasons, it was attributed to Gabriel del Barco (1649–*c.* 1703), a Spanish painter and tile decorator, and dated *c.* 1700 (Meco, 1989, 1994). The original length of the panel is yet unknown and the frame – very common in Portuguese decorative tile panels produced in the same period – has been lost (Castel-Branco Pereira *et al.*, 1992).

The panel was transferred to the National Tile Museum in 1960 and fixed to a mobile wooden support by applying a hot gluing process; it was later remounted over Plexiglas plates using silicone glue. The advanced degradation state of this impressive art piece motivated a consolidation treatment undertaken in 1990 using Paraloid™ B-72 (Rohm and Haas Company, Philadelphia, PA 19105, USA) (Castel-Branco Pereira *et al.*, 1992) with the aim of stabilizing the whole panel. Segments of the left and right panel extremities were then stored in the museum depository.

Materials and methods

This study is based on tile fragments removed from the top of a non-exposed panel segment stored in the depository of MNAz which display green stains irrespective of the coloring of the glaze, white or blue (Fig. 1A). Observed under a stereomicroscope, a small tile fragment shows that the green stains were located just at the glaze surface (Fig. 1B), without reaching the ceramic body (Fig. 1C).

X-ray techniques

Non-destructive X-ray techniques – X-ray diffraction (XRD) and X-ray fluorescence spectrometry (XRF) – were applied by directly irradiating the glaze of small tile fragments.

Table 1 XRF-WDS elemental data

Element	2 θ°	Tile glaze	Green stains
Background	134.00	984	585
K Kβ	118.15	13926	5870
Sn Lβ	114.40	7906	3520
Ca Kα	113.10	23391	15516
Ti Kα	86.14	1626	824
Background	84.00	286	191
Background	71.00	626	411
Cr Kα	69.36	700	680
Mn Kα	62.97	1463	1299
Fe Kα	57.52	32098	39761
Co Kα	52.80	2455	2957
Background	50.00	1410	1314
Ni Kα	48.67	2168	2370
Cu Kα	45.03	6107	3594
Zn Kα	41.80	6282	5047
As Kα + Pb Lα	34.00	447793	167327
As Kβ	30.45	3120	2477
Pb Lγ	24.07	38167	16863
Background	21.50	1775	1989

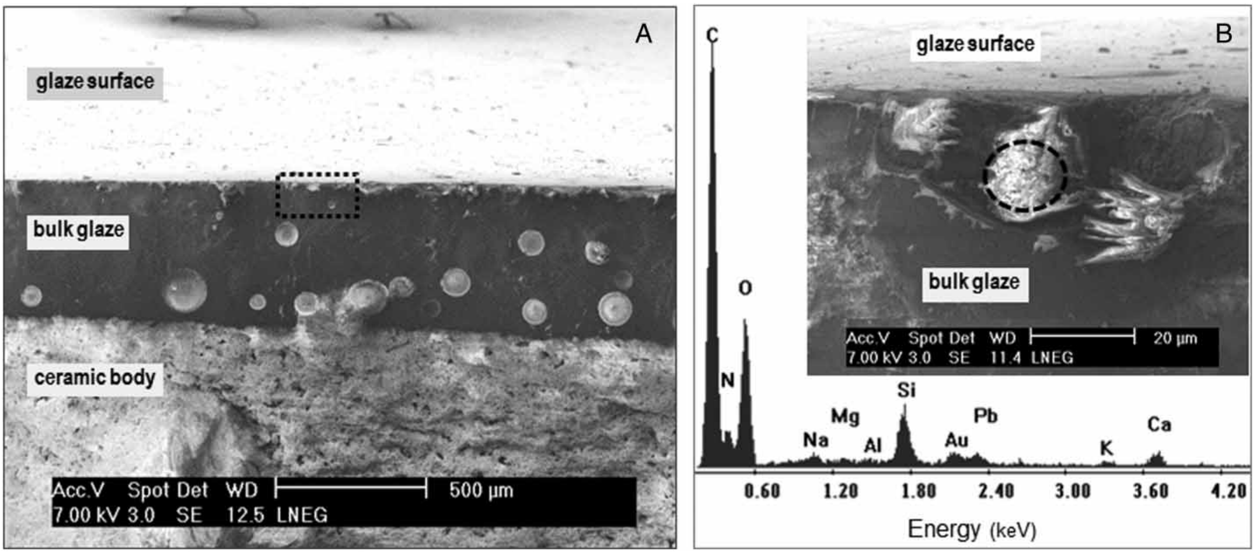

Figure 2 SEM images collected from the fragment reproduced in Fig. 1B: (A) profile view showing vacuoles within the glaze with a rectangle assigning the studied area; (B) detail of this area and EDX spectrum collected from an irradiated green stain (defined by a circle).

A Philips PW 1500 powder diffractometer with Bragg-Brentano geometry equipped with a large-anode copper tube and a graphite crystal monochromator was used to check the eventual development of new phases in the greenish areas as a result of degradation processes induced either on the white glaze or on the blue pigment.

Comparative chemical characterization of white and blue areas in the glaze and of green stains was performed using an automated Philips PW 1400

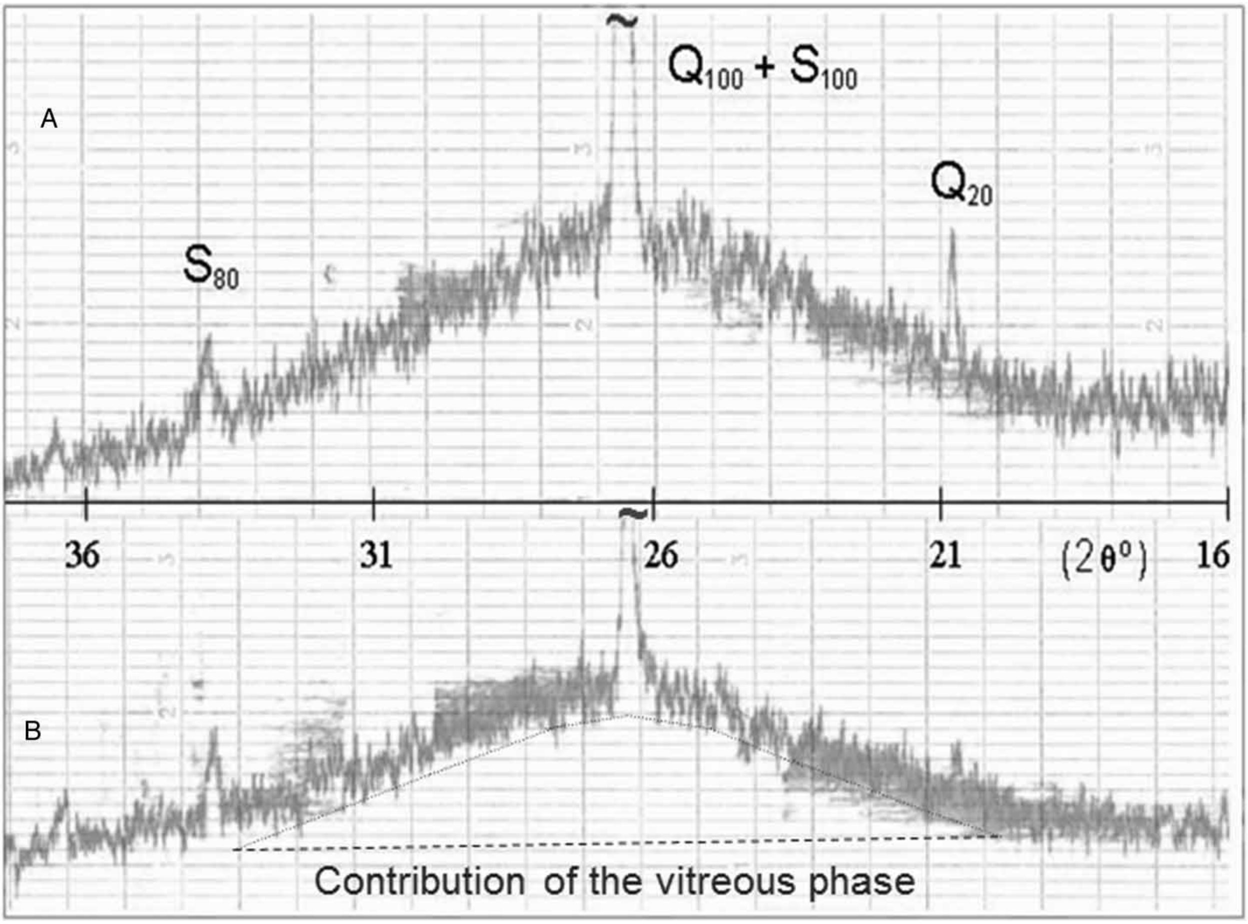

Figure 3 X-ray diffraction patterns obtained for irradiated areas in the studied tile fragment: white glaze (A); green stain (B); the relative intensities of assigned diffraction peaks from quartz (Q) and cassiterite (S) are indicated.

Table 2 Counting ratios calculated from XRF-WDS data

Ratio	Tile glaze	Green stains
Mn / Co	0.8	0.5
Fe / Co	29.4	23.4
Cu / Co	5.0	1.4
K / Ca	0.6	0.4
Pb / As	27.1	30.5

wavelength dispersive X-ray fluorescence spectrometer (XRF-WDS) with X-41 software and equipped with a rhodium tube. Fixed-time countings (5×10 seconds) were carried out over the diagnostic lines of relevant elements using a LiF200 analysing crystal. The Kα line of representative blue chromophore elements (Co and Cu) and glaze components (Ca and Zn), as well as of minor elements (Ti, Cr, Mn, Fe, and Ni), were used to carry out the countings, along with the Lα line of lead. To evaluate other glaze constituents, specific emission lines were selected, namely Kβ for potassium and Lβ for tin.

Owing to the superposition of Pb Lα and As Kα lines, the Kβ line of arsenic and the Lγ line of lead were also measured to correctly ascertain the presence of each one of these elements.

Averages of five measurements over each diagnostic line and over the corresponding selected background are listed in Table 1.

Scanning electron microscopy

Morphology and topography of studied samples were observed under a scanning electron microscope (SEM) Philips XL 30 FEG, with a field emission electron source operated at an acceleration voltage of 7 or 10 kV. Qualitative elemental analyses were performed with an energy dispersive X-ray spectrometry microanalysis (EDX) coupled to the microscope.

The detector is equipped with a 0.3-μm super ultrathin window allowing for the detection of elements with low-energy characteristic X-ray emission lines (e.g. carbon and nitrogen). X-ray emission spectra were collected in spot mode analysis (around 3-nm beam resolution) with 300 seconds acquisition time. For the SEM/EDX analyses, the samples were coated with gold in a JEOL ion sputter JFC-1100 to improve the imaging capability without interfering with the detection of carbon.

Spherical vacuoles are common in ancient glazes (Fig. 2A) and, if located at the surface, they frequently host newly formed degradation materials along with microorganisms (Fig. 2B).

Results and discussion

XRD patterns collected from green stained areas and from the blue-and-white glaze are identical (Fig. 3): beyond a diffuse contribution due to the vitreous component (a siliceous lead-rich glass; Figueiredo *et al.*, 2006), the crystalline phases present are quartz, α-SiO_2, and cassiterite, SnO_2 – the opacifier currently used to manufacture tile glazes in the seventeenth–eighteenth century (Figueiredo *et al.*, 2002). No additional crystalline phases stemming from glaze degradation could be detected.

Table 2 lists the ratios of fixed-time countings obtained by XRF-WDS for selected elements after subtracting the corresponding spectral background. No major chemical changes were assigned in the glaze due to the green staining for some representative metallic elements – Mn, Fe, and Cu plus Co, the blue chromophores. Conversely, the relative glaze contents of potassium vs. calcium decrease in the stained areas while the ratio of Pb/As increases to a noteworthy degree. This may well arise from the known

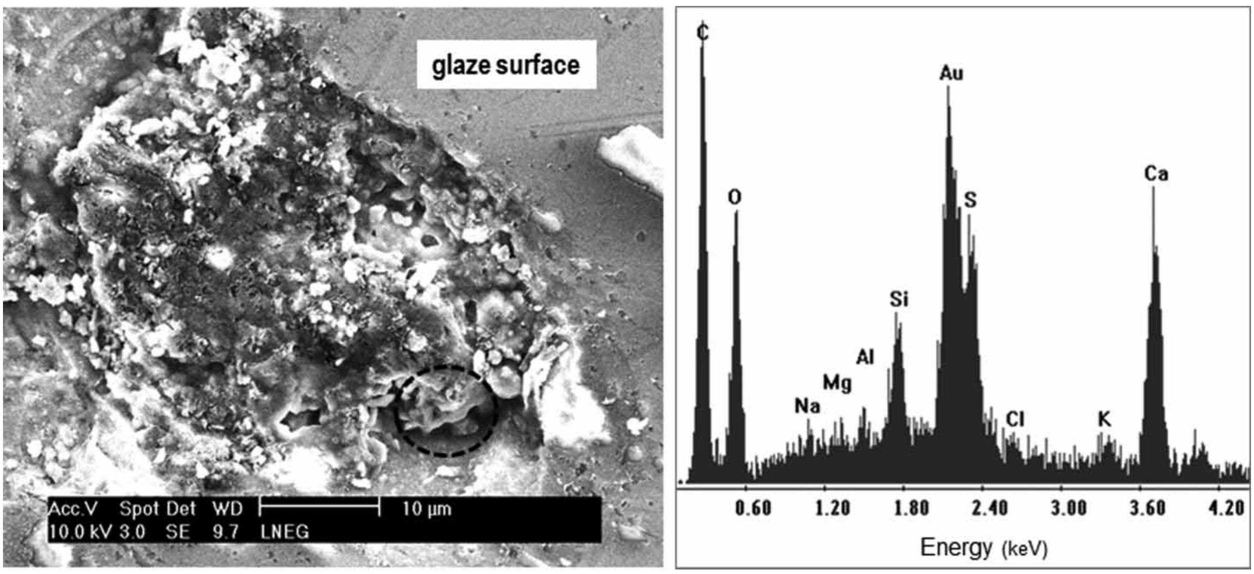

Figure 4 SEM image of a corroded area in the white glaze and EDX spectrum collected from the area defined by a circle.

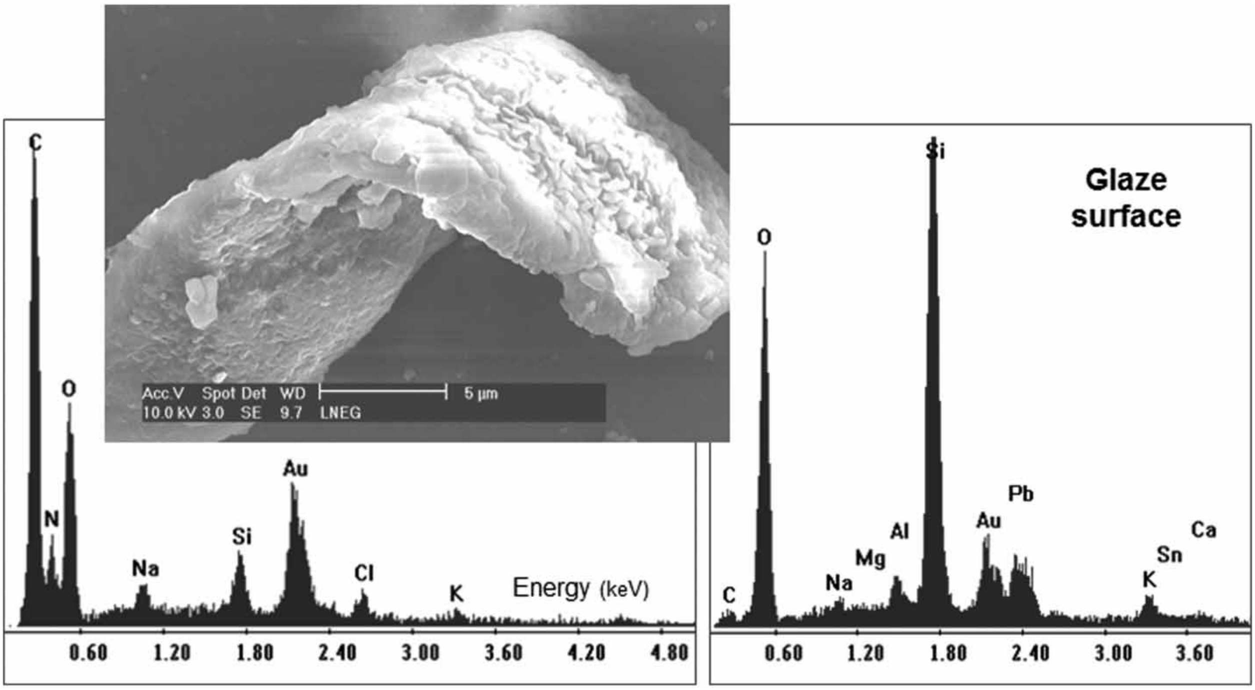

Figure 5 Comparison of EDX spectra collected from a microorganism and from the glaze surface.

aptitude of microorganisms to incorporate toxic metals (White *et al.*, 1995).

The intensity of carbon contribution to SEM-EDX spectra (Figs. 2B and 4) collected by irradiating green stains at the glaze surface conforms to the occurrence of microorganisms. The SEM image of such an organic specimen noticed at the glaze surface is reproduced in Fig. 5 and the corresponding EDX spectrum shows the presence of nitrogen beyond carbon when compared to the silicon- and lead-rich spectrum obtained from the glaze. As an attempt to identify the nature of these microorganisms – algae, fungi, or bacteria – samples will be prepared for laboratory cultures, particularly from algae mentioned by previous authors in relation with the degradation of glazed ceramic tiles (e.g. Oliveira *et al.,* 2001).

Conclusions

The present study confirms that the bulk constitution of blue-and-white glazes from seventeenth–eighteenth century tiles was not significantly affected – neither chemically nor in phase constitution – by the green staining due to microorganisms (algae?). These results are in agreement with previous observations concerning ancient blue-and-white glazes of Portuguese manufacture (Oliveira *et al.*, 2001; Figueiredo *et al.*, 2009), as well as with the staining observed in recently restored twentieth-century polychrome tiles subjected to intense humidity (Giacomucci *et al.*, 2011).

The noticed surface corrosion or pitting of this lead-rich glaze is understandable in view of the ability of microorganisms to uptake and concentrate toxic metals (White *et al.*, 1995), with emphasis on the recognized biosorption of lead by algae which is nowadays taken advantage of with technological applications (Gupta & Rastogi, 2008).

A smoky discolouration of the glaze noticed after irradiating the tile fragments for XRD and XRF-WDS analysis signifies that these non-destructive assays are nevertheless quite invasive temporarily. Thus, prior to any future application of tile conservation actions involving gamma radiation, further study is required to overcome anticipated color degradation of ancient glazes induced by the laboratory photonic assays.

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