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Ancient rendering mortars from a Brazilian palace
Its characteristics and microstructure

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Abstract

Rendering mortars of the *Cruz e Souza* Palace in Florianópolis City, SC, Brazil, built in the beginning of the century, are suffering from serious damage, such as detaching, crumbling, and cracking. The purpose of this work is to identify the components of the mortars in order to, if possible, reproduce the material in the damaged areas. Samples from two healthy regions of the rendering were studied: the first one from an ornament, a type of bracket that sustains the roof eaves of the palace, and the other one from a masonry rendering. Samples were characterized by X-ray diffraction (XRD), differential thermal/thermogravimetric analysis (DTA/TG), and scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDAX). XRD and DTA showed, in both cases, that the principal binder is a calcium carbonate present as calcite and vaterite in the first sample, and as calcite in the other. SEM showed two morphologies of calcium carbonate and the existence of an amorphous calcium hydrosilicate in the first case. An interpretation about the origin of these renderings is presented.

Keywords: Microstructure; SEM; X-ray diffraction; Thermal analysis; Ancient mortar

1. Introduction

The *Cruz e Souza* Palace, in downtown Florianópolis (Santa Catarina, Brazil), served as the official residence as well as the administrative building for various provincial presidents. Its construction began in the second half of the 17th century. Although it went through many restorations during the 19th century, the first attempts to restore the damaged areas were made in 1977. Afterwards, between 1984 and 1986, another attempt was made in order to restore the renderings of its walls and roof. However, in both occasions, no care was taken to restore of the elements to their original form. Technical data are inaccurate and incomplete. In 1997, a new restoration project was initiated, this time based on technical and scientific criteria of conservation and restoration.

Therefore, in order to know the materials employed in the original renderings, some mortar samples were extracted from the building and their physical-chemical characteristics were studied. The aim of the present work is to study the origins of two of these mortar samples.

2. Materials and methods

Samples were extracted from two healthy regions of the renderings. The first one is from an ornament-like bracket that sustains the roof eaves of the palace (termed as *bracket mortar*) and the second one is from a masonry rendering located on the northwest façade (termed as *rendering mortar*).

Samples were examined by X-ray diffraction (XRD) with a Philips powder diffractometer using CuKα radiation. For differential thermal/thermogravimetric analysis (DTA/TG) analysis, the temperature was raised at a constant rate (10°C/min) from ambient temperature to 1400°C in an atmosphere of nitrogen. For scanning electron

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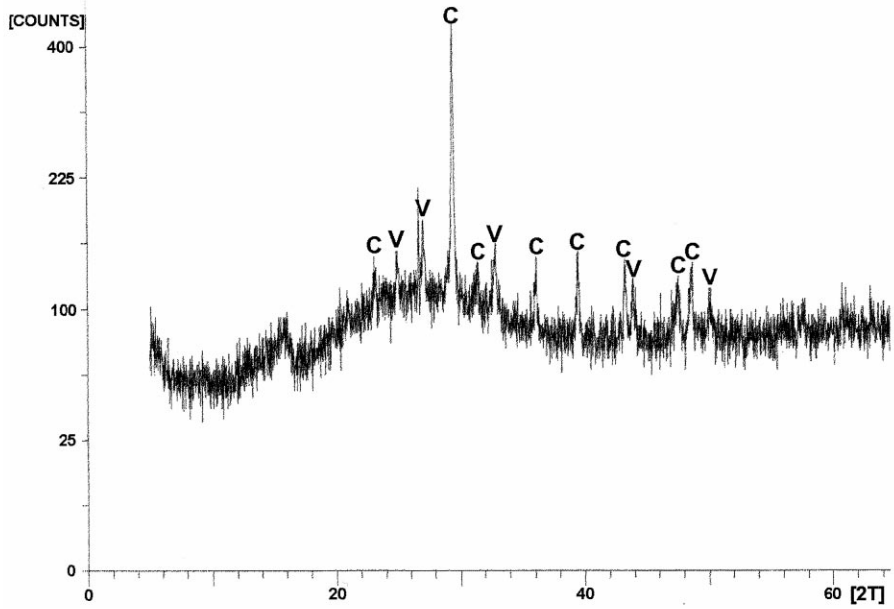

Fig. 1. XRD pattern of the bracket mortar (C = calcite; V = vaterite).

microscopy (SEM) observations, the samples were covered with a thin gold layer.

3. Results

3.1. General observations

The bracket mortar was a very dense material making the crushing process very hard. It shows no apparent aggregate. The rendering mortar was highly porous and contained fine aggregates, and was easy to crumble with the fingers.

3.2. Microstructural characterization of the bracket mortar

XRD analysis (Fig. 1) shows the predominant presence of calcium carbonate ($CaCO_3$) that coexists in two forms: calcite and vaterite. DTA (Fig. 2) shows the exothermic transformation of vaterite into calcite (nearly 450°C). Calcite that normally dissociates around 850°C [1] decomposed, in this case, at around 800°C. This is probably due to an imperfect crystal structure [2].

Nevertheless, there are other mortar phases that are difficult to identify, both in XRD analysis as well as DTA. For example, the DTA peak at about 830°C could be the transformation of a compound-like calcium hydrosilicate into wollastonite [3,4]; this observation can be confirmed by the existence of a few non-identified XRD peaks, proximate to interplanar distances (d_{hkl}) of some badly crystallized C-S-H gels [4] (see SEM characterization).

SEM observations show that various phases with different morphologies coexist as follows: a porous matrix (A zones in Fig. 3), large pores (diameters are from 20 to 250 μm) with internal filaments and walls with distinct morphology compared with the bulk paste (B zones in Fig. 3), and very dense zones that look like great "plates" (C zones in Fig. 3).

Fig. 4a shows the coexistence of two different morphologies in the porous matrix: the first one presents a laminar crystal structure (maximum length of 5 μm for a maximum thickness of 1/2 μm) and sometimes plates on edge (maximum length of 5 μm for a maximum thickness of 1 μm) identified by energy dispersive X-ray analysis (EDAX) as calcium carbonate in the vaterite form with traces of Si (Fig. 5b); the second structure is denser and less porous than the first one, and it is also composed of calcium carbonate with traces of Si but in the calcite form.

The detailed morphology of the large pores (Fig. 5a) exhibits a denser structure than the porous matrix described above. EDAX analysis (Fig 5b) of this structure also shows

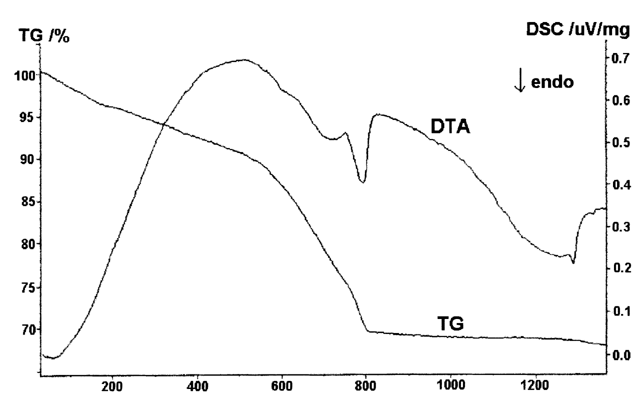

Fig. 2. DTA/TG pattern of the bracket mortar.

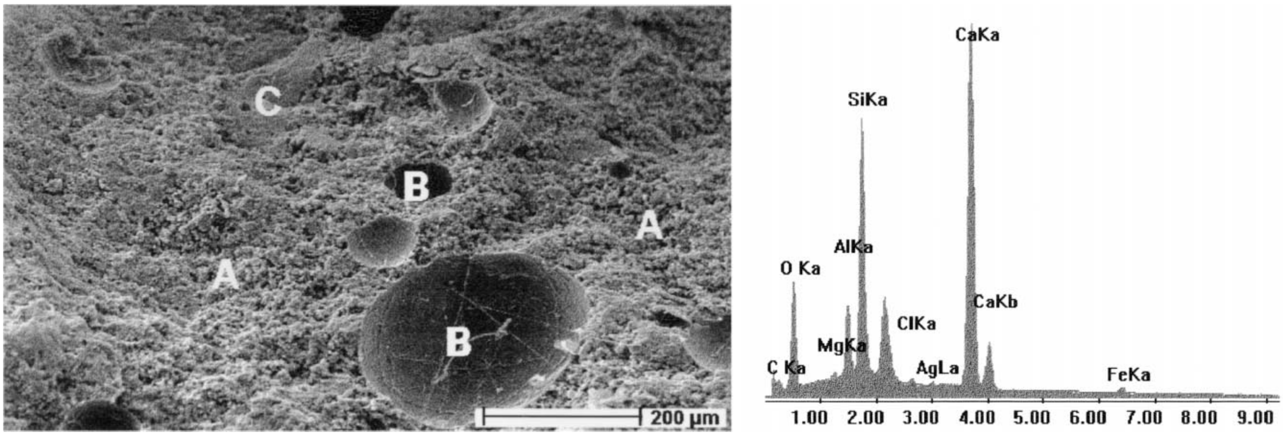

Fig. 3. (a) SEM micrograph of the bracket mortar showing large pores; (b) EDAX spectrum of the C zone.

a predominance of calcium carbonate and its denser morphology could be a consequence of the laminar crystal structure vaterite compacting due to the pressure exerted by the incorporated air.

The large filaments (length of up to 200 μm) observed inside the large pores are essentially composed of carbon; they could be filamentous fungi that developed itself afterwards (Fig. 5a).

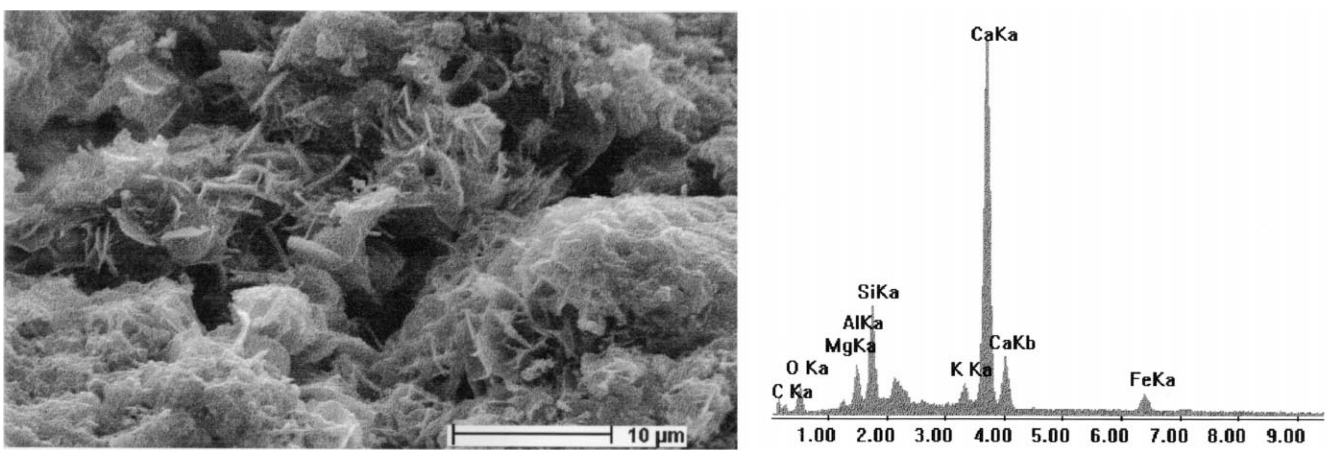

Fig. 4. (a) SEM micrograph showing the morphology of the calcium carbonate paste with denser zones (calcite) and laminar crystals zones (vaterite); (b) EDAX spectrum example of a laminar crystal.

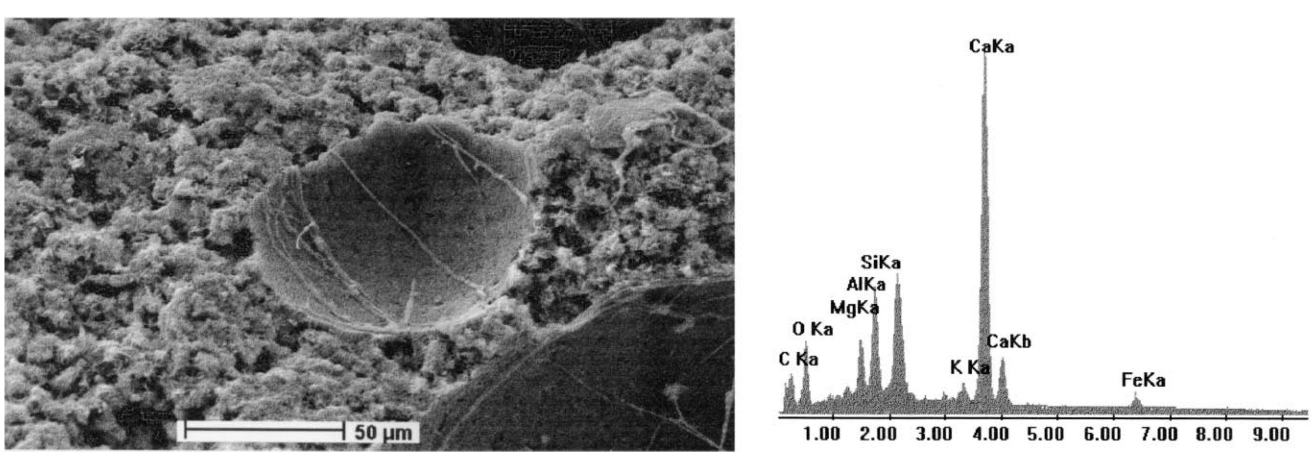

Fig. 5. (a) SEM micrograph of a pore with filaments; (b) EDAX spectrum example of a wall pore.

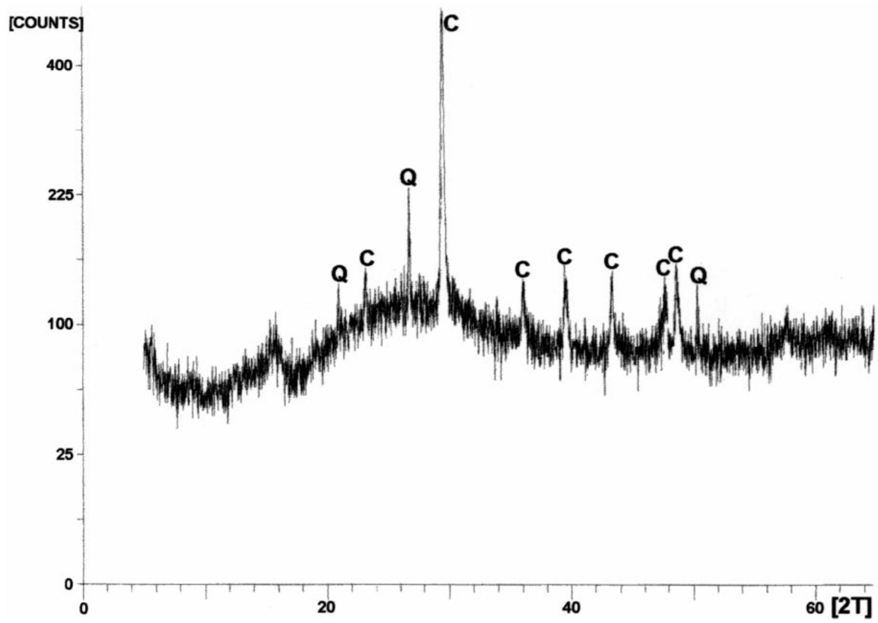

Fig. 6. XRD pattern of the rendering mortar (C = calcite; Q = quartz).

The denser zone morphology, described as large "plates" observed in Fig. 3a (C zone), is very abundant and well distributed in the bulk paste (length of up to 100 μm). They are composed of a kind of calcium hydrosilicate ($0.5 < Ca/Si < 1.5$; Fig. 3b) that is poorly crystalline and probably mixed with calcium carbonate [4].

3.3. *Microstructural characterization of the rendering mortar*

The rendering mortar XRD pattern (Fig. 6) shows the predominant presence of calcium carbonate as calcite and quartz. DTA (Fig. 7) confirms these results: endothermic transformation of the quartz α to β form occurs at about 573°C and the endothermic dissociation of poorly crystalline calcite occurs at about 780°C [2]. The other transformations above 1290°C would be due to the combination of silica with calcium oxide to form dicalcium silicate (C_2S) or/and monocalcium silicate (CS) [4].

SEM observations (Fig. 8) shows that the mortar is composed of a very porous binder and fine aggregates (maximum diameter 300 μm) mainly formed of quartz.

Fig. 9 shows the morphology of the mortar binder. It is formed by small agglomerated particles (diameter between 1 and 10 μm) and denser zones. It shows a lot of cracks and seems to develop a poor bonding with aggregates. EDAX analysis showed that the major compound is calcium carbonate as calcite with traces of Si and Mg (Fig. 9b). Fig. 9 also shows the existence of small rods, which were very well distributed in the bulk

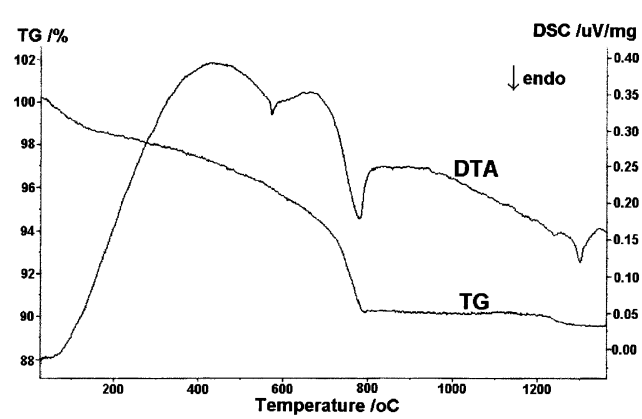

Fig. 7. DTA/TG pattern of the rendering mortar.

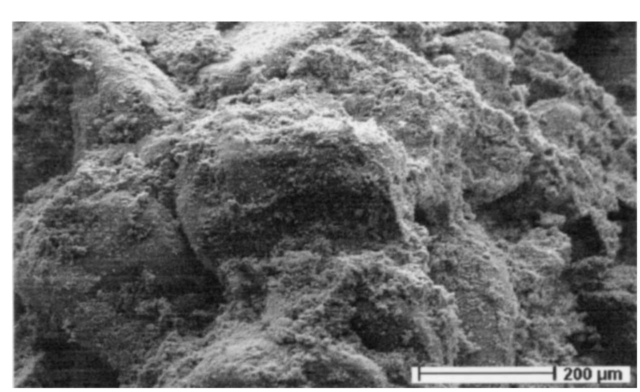

Fig. 8. SEM micrograph of the rendering mortar.

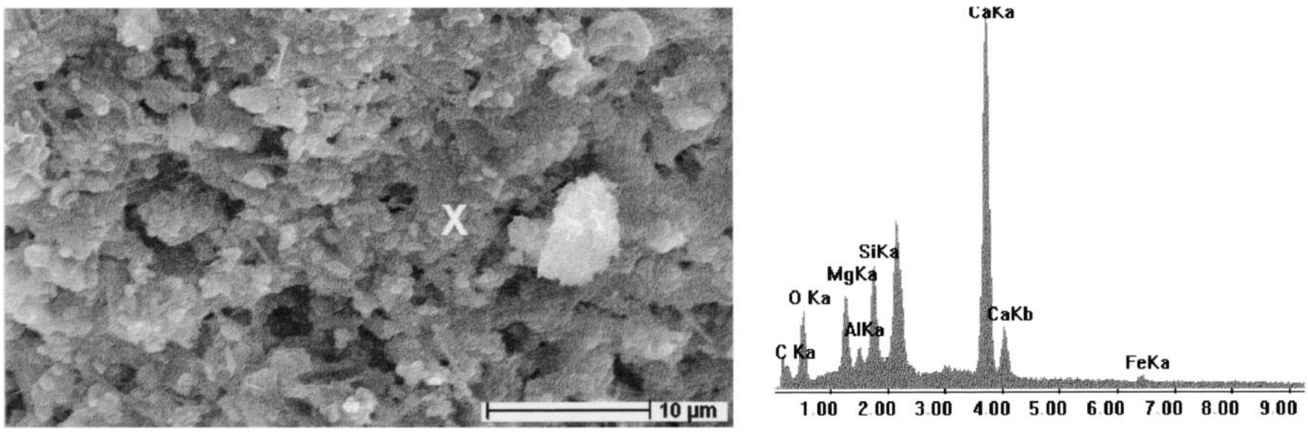

Fig. 9. (a) SEM micrograph of the binder; (b) EDAX spectrum example of the binder zone (marked with a X).

paste (maximum length of 5 μm for a maximum thickness of 1/2 μm).

4. Discussion

Up to the advent of Portland cement, at the end of the 19th century, the main important hydraulic binders were [5,6]:

(i) lime mixtures with volcanic pozzolans or ground burnt clay (finely ground bricks or tiles), already used in a large scale by the Romans, according to the following equations:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

followed by

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

and

$$Ca(OH)_2 + SiO_2 + H_2O \rightarrow CaO - SiO_2 - H_2O$$

that can be eventually carbonated as following

$$CaO - SiO_2 - H_2O + CO_2 \rightarrow CaCO_3 + SiO_2 + H_2O$$

(ii) artificial hydraulic lime, which was discovered at the beginning of the 17th century. It is the product of the burning of a clay-based material rich in alumina and silica with calcium carbonate giving highly hydraulic phases (e.g., dicalcium silicate):

$$2CaO \cdot SiO_2 + H_2O \rightarrow CaO - SiO_2 - H_2O + Ca(OH)_2$$

followed by

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

and eventually by

$$CaO - SiO_2 - H_2O + CO_2 \rightarrow CaCO_3 + SiO_2 + H_2O.$$

However, it seems that the use of artificial hydraulic lime was not very common as a substitute for lime-pozzolans mixtures, until the discovery of Portland cement [6].

Based on these data and on the microstructural characterization, we arrived at the following hypotheses about the origin of the mortars:

4.1. Bracket mortar

This mortar does not contain any aggregate (e.g., sand) and the presence of any clay-based material in its composition was not detected.

The presence of calcium carbonate suggests that one of the original mortar materials was a calcium oxide-based compound; this phase is basically composed of a poorly crystalline calcium hydrosilicate that suggests the presence of a pozzolanic material (amorphous silica) in the mixture.

According to the results of the analysis and the literature [5,6], two hypotheses can be given about the origins of this mortar:

1. mixture of lime (essentially composed of CaO but with traces of SiO_2, MgO and Al_2O_3) with a natural pozzolan (amorphous SiO_2);
2. use of artificial hydraulic lime essentially composed of $2CaO{\cdot}SiO_2$.

It is worth emphasizing that, from a practical point of view, hydraulic mortars used since the middle of the 18th century and containing hydraulic lime do not show, chemically and once hardened, any significant differences when compared with lime-pozzolans mortars developed by the Romans, since the reaction products are the same [5]. This fact makes the interpretation of the analysis difficult.

However, the utilization of artificial hydraulic lime seems unlikely because of its restricted use [6]. Besides, according to a survey on the historic research, during the period of the palace restoration (1895/1898), Santa Catarina state government would have imported "terra Romana" (Roman land), which is supposed to be a kind of natural pozzolan. Probably this material, added to local lime, could be the raw material used to make the referred ornaments.

4.2. Rendering mortar

This mortar basically contains fine aggregates (mainly quartz) and a calcium carbonate-based binder, but always with minor percentages of Si and Mg in its composition. A great number of iron (oxide)-based particles were observed, which give a red color to the mortar.

In this case, it can be supposed that the original binder used was lime with a high level of impurities (e.g., SiO_2, MgO, and Al_2O_3). It also seems clear, that contrary to the console mortar, pozzolan materials were not used with the lime.

5. Conclusions

Microstructural characterization is essential in order to know the origin of construction materials, especially in the case of historic buildings, where the aim of the restoration work must be to re-establish the original materials.

In the present study, through the characterization of two mortars used in the construction of the *Cruz e Souza* Palace, it was possible to conclude that:

the bracket mortar probably comprised a mixture of lime with imported pozzolanas ("terra Romana");
the rendering mortar was simply a mixture of lime and ordinary sand.

The non-existence of Portland cement in the composition is a strong sign that these mortars are original from the first restoration of the palace that occurred between 1895 and 1898.

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