## Historical glazes (14th-16th century CE) characterization for the development of adapted restoration materials in Morocco

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## Abstract

Historical Islamic monuments are impressive by their artistic and fascinating architecture, and many of them therefore belong to the UNESCO world cultural heritage. Particularly, in Morocco the historical monuments are carefully decorated with arranged glazed ceramic pieces, called "zellige", giving the buildings their typical and colorful appearance. The glaze performs a dual role in the decoration and protection of the surface. Unfortunately these architectural monuments lose their impressive appearance, when the glazed tiles are damaged and the glazes are chipped off (Fig.1). Through time, the influence of climate, water and environmental pollution can cause deterioration of the building materials and contribute to the chipping of the tile glazes (Tite *et al.*, 2016, Gradmann, 2016). Unfortunately this damage affects many historical buildings worldwide, and restoration of glazes becomes urgent to save the brilliant facades from irreversible destruction. In Morocco, eight sites located in the imperial cities Fez and Marrakech, were classified as world heritage by UNESCO in the sixties. Since then, restoration campaigns are being undertaken to preserve the former architecture of these monuments. However, two recent restoration campaigns undertaken in Marrakech have been unsuccessful, because of the weakness of the tiles used.



Fig. 1. Appearance of current damaged ceramic on the Saadian tombs (a) and the El Badi Palace (b).

This study aims to characterize the glazes of the main historical buildings (14th-16th century CE) in the Marrakech area with the purpose of developing adapted restoration materials. This study will contribute to selecting the most appropriate glaze composition for restoration purposes. To address this issue, a total of 156 glaze samples were taken. Among these, 27 samples are original to different buildings in the Marrakech and Fez area (Saadian tombs, Bahia Palace, El Badi Palace and Medersa Ben Youssef, 14th to 16th c. CE), 11

samples are assumed to belong to a 1<sup>st</sup> restoration phase, 18 samples are assumed to belong to a 2<sup>nd</sup> restoration phase and 97 samples are derived from recent traditional zellige production.

The glazes were carefully observed under a binocular to identify any damage affecting the surface of the sherds. The glaze color was determined using a Konica Minolta CM-700d spectrophotometer. Non destructive XRF devices (Thermo Fisher Scientific© Niton XL3t GOLDD) were used to determine the chemical composition of the glaze. Mineralogical phases of different color of glazes were carried out using a BrukerD8-Advance diffractometer with copper anticathode.

From 14th to 16th century CE, in Marrakech area, the ceramists use a mixture of clay, sand and flux agents to manufacture glazes. The chemical composition did not highlight obvious correlation between the colors of the glazes and their compositions, except for the green colored glaze. The latter contains copper and sporadic chromium as a colorant. The historical glazes are lead glazes with Pb contents from 37 to 56%, opacified with Sn in the range 4–18%. Our results are in agreement with the composition of Islamic glazes in the Mediterranean area in general, and in Southern Spain in particular (e.g. Molera et al., 2001, Gradmann, 2016). This technology is taken up from the Roman and Byzantine imperia and then continued during the medieval Islamic culture in Morocco. The use of lead as flux, in association with alkalis, promotes the expansion properties during firing and increases the hardness of the tile and makes the color more clear. Furthermore, the glaze appears thicker with a more brilliant color, due to the high diffraction index of lead glass (Tite et al., 1998). In recent glazes, however, a decrease in lead amount is observed for the two restorations phases, reflecting the weakness of the glazed tiles mainly with the lack of any substituent of flux agent (Fig. 2a).



Fig. 2. (a) Pb and Cu content of the colored glazes. The green glaze contains Cu mixed with lead. Also noted is a decrease in Pb content in the recent glazes. (b) Ternary diagram Pb-Si-flux (Ca-Fe-Mg-K) indicating the decrease of Pb amount used for restoration of the El Badi Palace. This reduction of Pb is not associated with any supply of flux, implying the partial melting at low firing temperature and then the weakness of the glazed tile.

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