Environmental influences on historical monuments:
a multi-analytical characterization of degradation materials

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Abstract

The Minoan Palace of Knossos and the Venetian coastal fortress “Rocca a mare” (Koules), located in Heraklion, Crete, Greece, are two important monuments for the history of mankind particularly vulnerable to environmental conditions, since they are located in an island subjected to strong variations in humidity and, as in the case of the Venetian fortress, in direct contact with sea water. In this type of surrounding environment, the formation of salt efflorescence as well as various other soluble salts crusts is a common situation. They occur according to the existing solubilization and crystallization conditions and can happen either in exterior or interior areas of the monuments. Their presence may stimulate further degradation, either due to the chemical dissolution of the substrate materials or due to the mechanical actions created by the formation of crystals, which may result in the decay of the substrate.

A set of samples from both monuments were analysed using various laboratory (ex-situ) analytical methods such as optical microscopy (OM), X-ray diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR), Raman spectroscopy and Laser-Induced Breakdown Spectroscopy (LIBS). In-situ measurements using portable Raman and LIBS instruments were also performed. The comparative results from ex-situ analysis and in-situ measurements will be presented with emphasis to the chemical composition of the crusts and their origin. Results indicate that observed stalactites and salt efflorescence are directly related to the type of supporting material and the conditions of the surrounding environment. In general, the formation of crusts and salts are due to processes of alteration of the supporting material while the high impact of sea salt on the formation of the efflorescence at the Venetian coastal fortress was also confirmed.

Results

White Crust, Stalactite and Efflorescence

Palace of Knossos

In-situ Characterization

White Crust

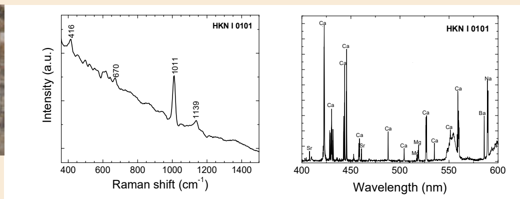


Figure 1: μ-Raman in-situ analysis identified Gypsum ($CaSO_4.2H_2O$), while LIBS additionally indicated the presence of Sodium (Na), Calcium (Ca), and other elements in minor quantity.

Efflorescence

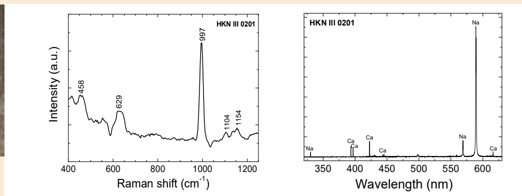


Figure 2: μ-Raman in-situ analysis identified Thenardite (Na_2SO_4), while LIBS indicated the dominant presence of Sodium (Na), as well as Calcium (Ca) in minor quantity.

Two types of samples collected:

White Crust samples

Efflorescence samples

Figure 3: OM, dark field, 10x. The white crust samples present some translucency grains, although visually distinct. Efflorescence samples present similarities in hue, heterogeneity and grain size.

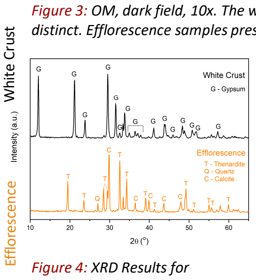
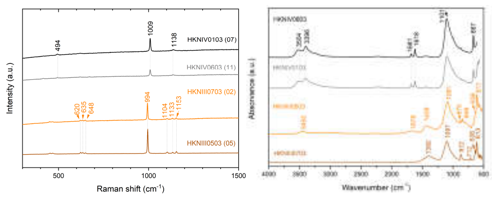


Figure 4: XRD Results for two different types of samples collected at the Palace of Knossos.



Figures 5 and 6: Raman and FTIR results identified Thenardite as the main component of the Efflorescence samples (orange lines). In that case, the FTIR results present also Calcite (sample HKNIII0703).The samples of white crust (grey and black lines), present the typical Gypsum band vibrations as the main component of this set of samples.

Koules Fortress

In-situ Characterization

White Crust

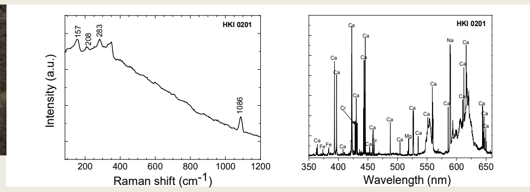


Figure 7: μ-Raman in-situ analysis identified Calcite ($CaCO_3$) and Aragonite ($CaCO_3$), while LIBS indicated the dominant presence of Sodium (Na) and Calcium (Ca), and others elements in minor quantities.

Stalactite

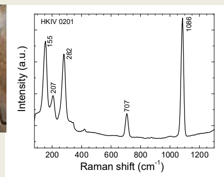


Figure 8: μ-Raman in-situ analysis identified two forms of $CaCO_3$: Calcite and Aragonite

Efflorescence

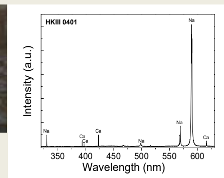


Figure 9: LIBS analysis indicated the dominant presence Sodium (Na), as well as Calcium (Ca) in minor quantity.

Three types of samples collected:

White Crust samples

Stalactite samples

Efflorescence sample

Figure 10: OM, dark field, 10x. There are similarities in the characteristics observed between the sample groups, such as the brightness and the translucency of some crystals.

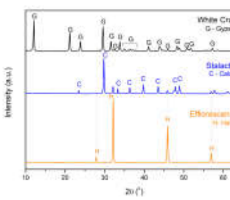


Figure 11: XRD Results for three different types of samples collected at the Koules Fortress.

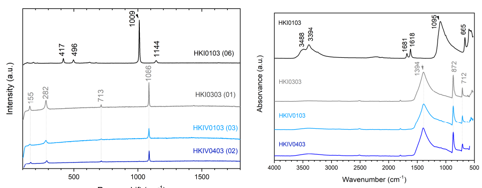


Figure 12 and 13: The results obtained by Raman and FTIR present Calcite as the main component of the Stalactite samples (blue lines). The samples of white crust (grey and black lines), in addition to gypsum, were also identified as calcite in some samples, which indicates a greater variation of composition for this set of samples and the influence of the support material.

Acknowledgements

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Final Remarks

White crusts, stalactites and salt efflorescence are directly related with the type of supporting material and the conditions of the surrounding environment. In general, the formation of crusts and salts are due to processes of alteration of the supporting material. However, in the case of Koules Fortress what is verified is that the sea salt and its location by the sea line has a more intense impact on the formation of the efflorescence. Although the Palace of Knossos is also located near the sea (6 km), the impact of marine salt is different from that observed in Koules, prevailing the formation of thernadite resulting from the deterioration process of the supporting material (cement).