Study and analyses of pigments in minoan larnax from the peripheral unit of Rethymnon (Crete) applying non-destructive techniques

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Introduction

From the beginning of the LM III A1 (1400-1375 BC) period there is a significant increase in the residential settlements in Crete, which is concluded from the corresponding increase in the number of tombs and seems to be a general phenomenon on the island, that reflects changes in burial customs. The type of underground chamber tomb prevails in majority, while burials inside larnakes, stretchers or beds is documented.

In peripheral unit of Rethymno, where the larnakes presented in this article come from, two very important, organized cemeteries of this period have been unearthed: the first one is at Mezaria in Maroulas, which is located 8 km SE of the city of Rethymno, and the second one is at Prinokefalos in Armenoi, which is located 10 km south of the city of Rethymno and is the most known cemetery of LM III A-B periods (LM IIIA1, 1400-1375 BC - LM IIIA2, 1375-1300 BC, LM IIIB, 1300-1200 BC) in Crete till now.

The number of clay-made larnakes coming from these cemeteries is important, which bear painted decoration and their motives can be divided into 4 groups: (a) abstract patterns, (b) representation of ritual scenes and events, (c) plants and animals devoted to a deity and (d) scenes from the afterlife. Most of the larnakes have red, black, white and yellow colors on their surfaces, and on two of the Armenoi cemetery the use of the grey-blue color is observed.

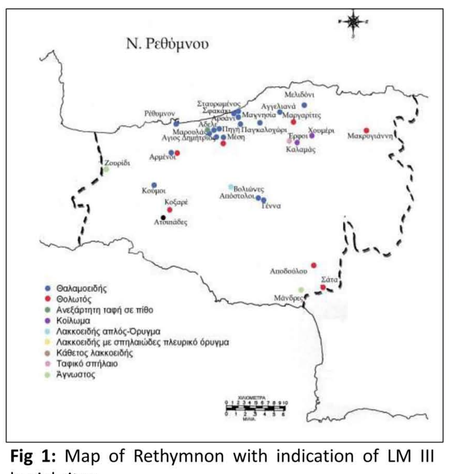

Fig 1: Map of Rethymnon with indication of LM III burial sites.

Fig 2: Armenoi cemetery.

Fig 7: Polychrome Larnax (1709) from Armenoi cemetery.

	XRF Results		
	Colour/ Visual Observation	Chemical Elements detected (%)	Chemical Elements detected (ppm)
1709	Black (inner part of the larnax body)	Ca, Ti, Fe, Mn	Cr, Ni,Cu, Zn, As, Rb, Sr, Y, Zr, Nb, Pb
	Red (from the body of larnax)	Ca, Ti, Fe, Mn	V, Cr, Ni,Cu, Zn, As, Rb, Sr, Y, Zr, Nb, Sn, Pb
	White (from the body of larnax)	Ca, Ti, Fe, Mn	V, Cr, Ni,Cu, Zn, As, Rb, Sr, Y, Zr, Nb, Sn, Pb
	Blue/Grey (from the body of larnax)	Ca, Ti, Fe, Mn	V, Cr, Ni,Cu, Zn, As, Rb, Sr, Y, Zr, Nb, Pb
	Blue/ Grey (from the narrow side of the body)	Ca, Ti, Fe, Mn	V, Cr, Ni,Cu, Zn, As, Rb, Sr, Y, Zr, Nb, Sn, Pb
	Red (from the lid)	Ca, Ti, Fe, Mn	V, Ni,Cu, Zn, As, Rb, Sr, Y, Zr, Nb, Pb
	Black (from the lid)	Ca, Ti, Fe, Mn	V, Cr, Ni,Cu, Zn, As, Rb, Sr, Y, Zr, Nb, Pb
	Blue/Grey (from the lid)	Ca, Ti, Fe, Mn	V, Cr, Ni,Cu, Zn, As, Rb, Sr, Y, Zr, Nb, Pb

Fig 8: XRF Spectroscopy Results.

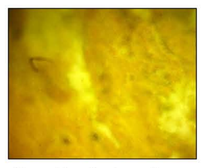

Fig. 9: Red colour with traces of blue and white pigments

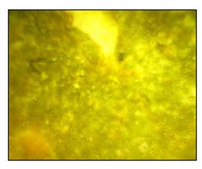

Fig. 10: Blue-grey colour with traces of blue, red and white pigments

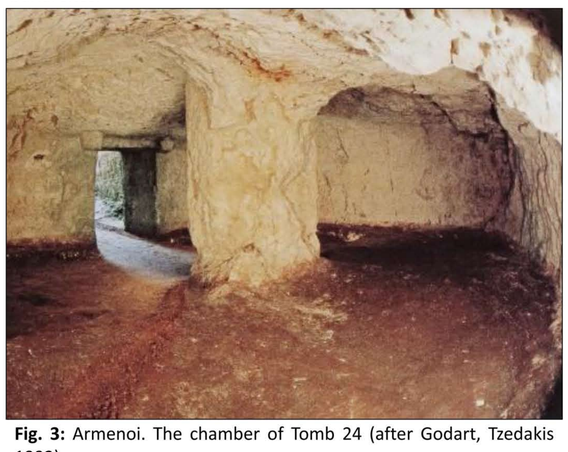

Fig. 3: Armenoi. The chamber of Tomb 24 (after Godart, Tzedakis 1992).

Fig. 4: Armenoi. Burial representation (after Godart, Tzedakis 1992).

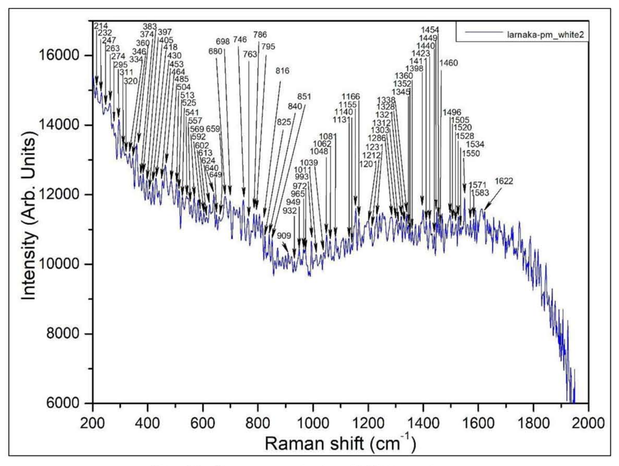

Fig. 11: Raman analysis of White colour.

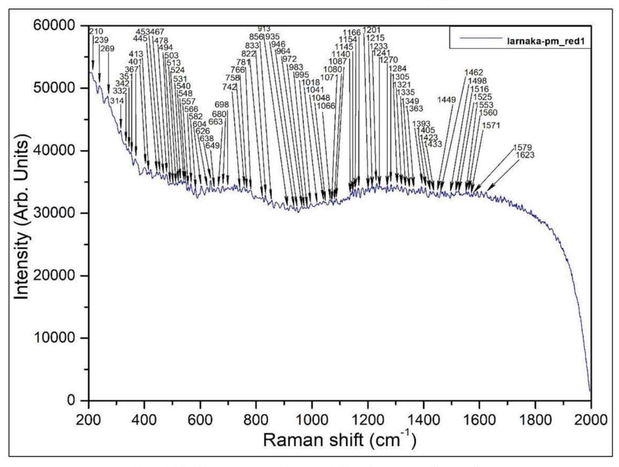

Fig. 12: Raman analysis of Red colour (body).

Experimental work

In the context of this announcement, the archaeometric examination of the pigments in larnakes with painted decoration, from various places of the peripheral unit of Rethymno, was attempted, the majority of which is dated from 1400 to 1190 BC. The main concern of this research was to determine the types of the pigments that were used to decorate the larnakes, but also, to observe if there are any differences in the use of colors, which may be due to the different workshops that constructed the larnakes or due to different ideological perceptions of the societies during this period, for the use of colors in objects that were intended for burial use.

A total number of 175 measurements were taken using X-ray fluorescence spectroscopy (XRF) on larnakes (bodies and covers), to determine if identical dyes had been used to decorate the box and the lid. At the same time, 108 measurements were taken mainly in the boxes of the larnakes using the Raman spectroscopy, due to the limited time, that we had at our disposal to conduct the research.

For the determination of the pigment compounds, the Portable RockHound 785 spectrometer of the DeltaNu house with attached NuScope optical microscope was used. Lazer, selected, had a wavelength of 785 nm with a 35 micron radius, a resolution of 10 cm^{-1} and a range of 200-2000 cm^{-1}. Correspondingly, for the elemental analysis of pigments, the Skyray portable XRF EDX pocket III spectrometer was used with S (16) to U (92) data detection ranges.

The duration of each measurement using the RockHound 785 spectrometer was in the range of 2-5 minutes, and no Raman spectrum was then processed. The analysis of the Raman spectra was done using the OriginPro software, while the identification of pigments with the Clark and RRUFF database.

Measurements using XRF spectroscopy had a maximum of 20 seconds and due to a technical problem that occurred during the measurements and which we were unable to solve, it was not possible to transfer the data to a computer. As a result, the instrument display data on the PDA unit screen was recorded using a digital camera, but without the possibility of subsequent processing of the XRF spectra.

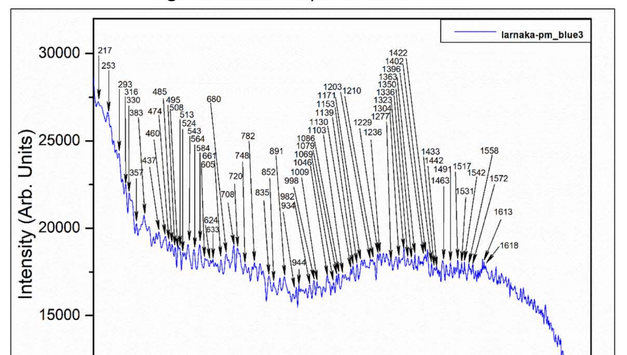

Fig. 13: Raman analysis of Blue/Grey colour.

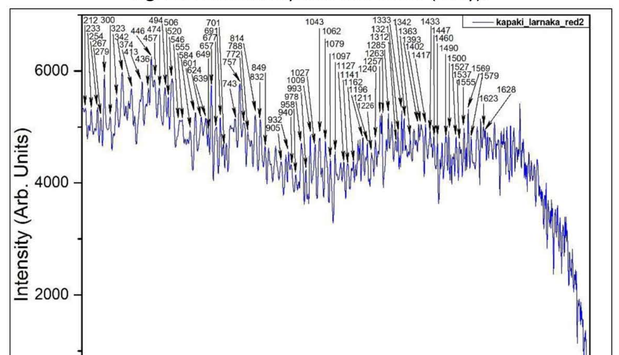

Fig. 14: Raman analysis of Red colour (Lid).

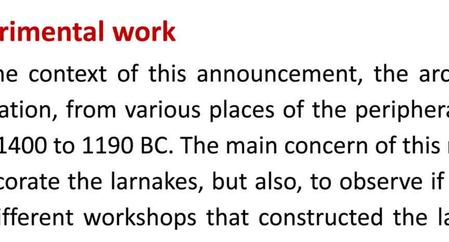

Fig. 5: Archaeometric examination with pXRF.

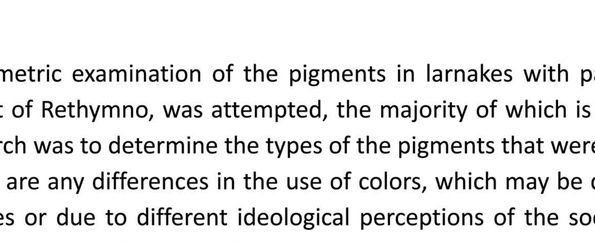

Fig. 6: Archaeometric examination with Raman spectroscopy.

Measuring results

The archaeometrical examination of the larnakes pigments by the use of Raman and XRF spectroscopy, indicated the presence of the following pigments: lead white, chalk white, gypsum white, bone white, ochre yellow, orpiment, red ochre, red lead, cinnabar, realgar, carbon black and bone black, azurite, riveckite, egyptian blue, malachite and green earth. Also, the organic pigments purpurine, berberine and saffron were identified, which due to their organic composition were confirmed only after using the Raman method.

From the total colours examined, we believe that gypsum white was used as the main colour in all the larnakes, while to a lesser extent the chalk (calcite), lead and bone white. The colors above seem to have been used both as a substrate for the subsequent color decoration of the larnakes and for the rendering of appropriate tonal gradations. In addition, gypsum white may have been used due to its properties and as a binder to stabilize the colors on the surfaces of the larnakes.

The red pigments that were measured in all larnakes with Raman spectroscopy are ochre red, realgar, cinnabar, lead red and purpurine. As a whole, they were identified mainly as basic colors to achieve bright and stable shades of red, which is found on the surfaces of the larnakes with shades ranging from light red-orange to dark red-brown-red colour.

The black pigments that were traced in almost all measurements with Raman Spectroscopy were used either as basic colors or as mixtures for the tonal gradient of colors, are carbon black and bone black. The black of the carbon could not be confirmed with XRF spectroscopy, while on the contrary the black of the bones is confirmed by the presence of Ca in all measurements.

The blue pigments traced in most of the measurements are azurite, egyptian blue and ribeckite. The aforementioned colors, with the exception of ribeckite, which was traced in only four blue/grey colour measurements, are presented with slight variations in most of the colors which were analyzed, mainly as mixtures to achieve appropriate shades.

Finally, the green pigments traced as mixtures in the measurements of red, black and blue-gray colour, as well as random mixtures in the measurements of white and yellow colour are malachite and green earth, the existence of which is also known to us from other places in Crete, such as Phaistos, where it has been found as a mixture in red mortar color, so as to give a brighter result.

Conclusions

Summarizing, according to the data provided by the measurements, with the use of the spectroscopic methods Raman and XRF, it is established that in all measurements, a variety of pigments is identified, that were used either as basic colors for the depiction of white, yellow, red, black and blue-gray or as randomly caused mixtures or dyes of secondary importance for depicting gradually toned hues, as well as stable overlay colours.

Additionally, in all the measurements taken with Raman spectroscopy, approximately, the same presence of various inorganic and organic pigments was found in all measurements of red, black, white, yellow and blue-gray, the existence of which was largely confirmed by the results of the X-ray fluorescence spectroscopy (XRF). The presence of a variety of pigments in most colors is also justified by the presence of overlapping layers of different colors, as it is reflected in photographs taken by the Raman instrument microscope during the measurement of the colors in larnakes.

Moreover, the presence of valuable raw materials in the colors of the larnakes, such as realgar and orpiment, azurite, egyptian blue, as well as cinnabar, which are all listed -as they are not found as raw materials in Crete-, should be commented on. Of these, the use of egyptian blue and azurite in objects and frescoes of the period from Crete is well known, while recently the use of orpiment and realgar was confirmed both in fragments of frescoes from Knossos and in pigments that decorate vases and figurines from Peak Sanctuary of Vrysina in Rethymno.

Also, noteworthy is the discovery in most of the measurements of three organic pigments, which come from plants that thrive in Crete and in particular these are purpurine, berberine and saffron. The aforementioned pigments have recently been found in objects from Rethymno, while purpurine has also been found in fragments of frescoes from Knossos. So, now we know, that except from inorganic pigments, native plants have also been used in the island, that produce cheap and easily accessible pigments.

To conclude, it should be emphasized that the results provided by the non-destructive spectroscopic methods of Raman and XRF were particularly remarkable and in the majority of the measurements, these spectroscopic methods proved to be suitable for both the determination of the chemical compounds of the pigments and the elementary analysis. The advantages of the two above-mentioned methods recognized the insignificant preparation of the objects before the measurement, their rapid analysis, as well as the provision of information that could not be obtained from methods that required sampling.

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