



NEW DATA ON THE CATHODOLUMINESCENCE OF WHITE MARBLES: INTERPRETATION OF PEAKS AND RELATIONSHIPS TO WEATHERING

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ABSTRACT

This work focus on the Thermoluminescence (TL), the Spatially Resolved Spectral Cathodoluminescence (CL) and Raman spectroscopy (Raman) of white marble specimens collected from the archaeological park of Aiani (Greece) and from patterns of Iceland calcite and Macael marble for comparison purposes. The spectra CL were measured with a high sensitivity cathodoluminescence spectrometer MonoCL3 of Gatan (UK) attached to an FEI-ESEM microscope (CL-ESEM). The experimental set of spectra CL curves of Aiani white marbles suggest that the blue band is more resistant to weathering in comparison with the red band which drops down easily under weathering. The comparison among CL spectra of CaCO₃ patterns give a slight difference between the small 330 nm peak, detected in marble and not observed in the monocrystal pattern of Iceland calcite. The Backscattering Electron Dispersed (BSED) images of the white marble are similar to the CL monochromatic plots at 330 nm which highlight the surfaces with remarkable clarity, suggesting a CL emission-defect associated to the marble crystal interfaces, such as protons or hydroxyls. Conversely, the 395 nm monochromatic mapping depicts a CL image emitting from bulk and not from interfaces attributable to point defects or cationic activators in Ca²⁺ positions. The blue band of the spectra luminescence of marble is composed by several peaks associated to very different types of luminescent defects. This statement is not inconsequential since in archaeological TL dating of marbles the regenerated luminescence in the blue region of the spectrum is a serious difficulty and further research on this topic is necessary.

KEYWORDS: Marble, Cathodoluminescence, Raman, Thermoluminescence, 330 nm, Aiani

INTRODUCTION

The spectra luminescence scientific background on calcite and marble is large, e.g., the orange-red emission has been observed in almost 100% of calcites analysed (Gorobets & Rogojine, 1981; Gaft et al., 2005). The main luminescence activator in carbonates is Mn^{2+} emitting in the red region of the spectrum, this is explained by the energy advantage of its incorporation into the calcite lattice forming mixed crystals $(Ca,Mn)CO_3$. Occasionally Rare-Earth Elements produce strong luminescence in calcite such as Ce^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} and Eu^{2+} . A previous preliminary provenance study of marble artefacts from Aiani, ancient Upper Macedonia, Greece (Iordanidis et al., 2008) showed that Tranovalto marbles situated in the south of Aiani, where some modern white marble quarries occur, could be the most probable origin of these white marbles. Aiani is located approximately 20 km to the South of the city of Kozani, Western Macedonia (Greece).

Aiani was within the region of the ancient Kingdom of Elimeia which, together with the rest of the Greek Kingdoms (Tymphaia, Orestis, Lyncestis, Eordaia, Pelagonia) constituted the ancient Upper (i.e. mountainous) Macedonia. The systematic excavations which began in 1983, have revealed the architectural remains of both large and small buildings, rich in small finds; and groups of graves and organized cemeteries dating from the Prehistoric to the Late Hellenistic period. The clusters of graves and the extensive cemeteries, which have been discovered and partly excavated around the ancient city, date from the Late Bronze Age to the Late Hellenistic Period. The excavations in the Archaic and Classical necropolis revealed twelve chamber-tombs, smaller cist-graves and numerous pit-graves. Aiani was a well-organized city from the Late Archaic to the Classical period (early V-IV c. BC; the VI c.) with direct cultural exchange with the rest of Greece.

The marble dating by TL routines the dating implications from solar bleaching of TL of ancient marble were initiated first by Liritzis & R. B. Galloway (1999) and Liritzis (2001). It is well known that TL of marble drops by sun exposure; moreover Polikreti (2003) observed that marble specimens exposed to sunlight show increased regenerated TL intensities after short or long period storage. This physical process requires a previous study of the regenerated TL evolution with time as a necessary step to estimate the error induced in age calculations. Simultaneously, Galloway (2003) performed an empirical study of luminescence around 360 nm from $CaCO_3$ (limestone) concluding that the results does not behave in a way that could be exploited for dating.

In addition, in other poly-grained carbonates, we observed this frequent 320-340 nm emission band attributable to non-bridging oxygen defects produced by dehydration e.g., Smithsonite (Garcia-Guinea et al., 2009a), Strontianite (Garcia-Guinea et al., 2009b). This statement is not inconsequential since in archaeological TL/OSL dating of marbles the regenerated luminescence in the blue region of the spectrum is a serious difficulty. Polikreti & Christofides (2009) performed photoluminescence to study the role of humic substances in the formation of marble

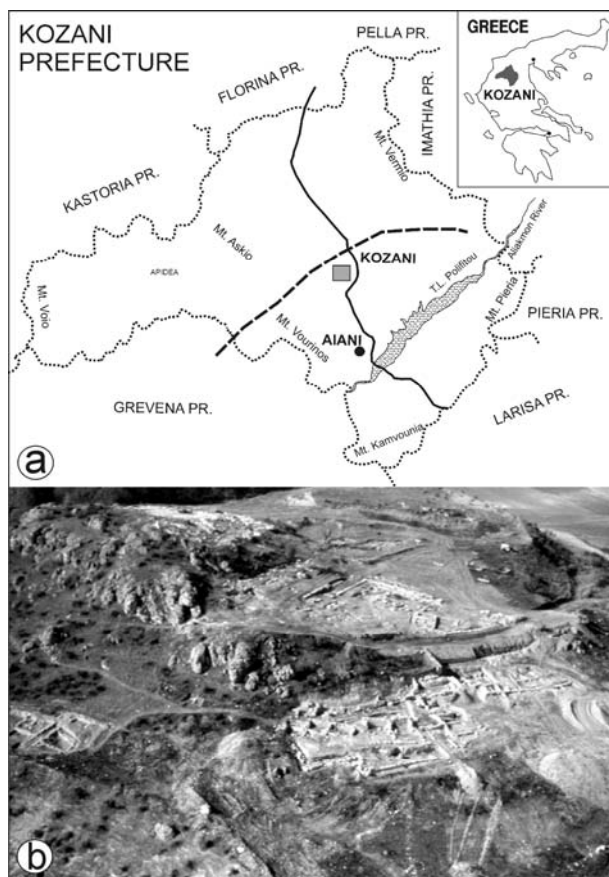


Fig. 1: Ancient city of Aiani (Greece): (a) Geographic situation in the modern Kozani Prefecture, (b) Aerial view of the archaeological park of Aiani.

patinas, unfortunately they used an excitation laser source at 363 nm and the lower spectra 330 emission peak could not be observed. Assuming that the TL heating dehydrates marble specimens producing 330 nm emissions, later marbles could rehydrate regenerating this spectra blue emission at circa 330 nm.

SAMPLING AND METHODOLOGY

The marble samples here studied were collected during archaeological works in Aiani (northern Greece), and include material scraped off from a statuary objects (samples AK, 10494, 10541, 10545, 10554 and 10563). Fresh marble samples were also collected from modern quarries or recent outcrops, situated in the vicinity of the Aiani archaeological area. Additional transparent Iceland spar from Gallarta (Spain) and fresh white marble from Macael (Spain) were also employed as control patterns in the luminescence experiments. TL measurements of powdered aliquots of the marble samples were performed using an automated Risø TL system model TL DA-12. This reader is provided with an EMI 9635 QA photomultiplier, and the emission was observed through a blue filter (a FIB002 of the Melles-Griot Company) where the wavelength is peaked at 320–480nm. Full-width at half-maximum (FWHM) value is 80716 nm, and peak transmittance (minimum) is 60%.

All the TL measurements were performed using a linear heating rate of 5° C/s–1 from room temperature up to 500°C, in a N₂ atmosphere. The incandescent background was subtracted from the TL data. The spectra CL were measured with a high sensitivity cathodoluminescence spectrometer MonoCL3 of Gatan (UK) attached to an FEI-ESEM microscope, CL–ESEM). The MonoCL3 system collect, disperse, measure, and record very low intensity CL signals.

The CL302 collection/retraction system has a precise XYZ positioning allowing a hole in a diamond turned parabolic mirror to be positioned coincident with the electron optical axis of the microscope. When a specimen emitting CL is positioned at the focal point of the mirror, light from the specimen is collimated and is either directly focused onto the detector, or else is coupled into the mono-chromator through

entrance slits. When optimised, the parabolic mirror can collect up to 75% of all light emitted by the sample. The CL-ESEM coupling allows recording high sensitivity spectra CL from spots, lines or squared areas and to perform monochromatic and panchromatic plots.

RESULTS AND DISCUSSION

Experiment 1.-

During a preliminary provenance study of marble artefacts from Aiani, ancient Upper Macedonia (Greece) (Iordanidis et al., 2008) a simplistic luminescence model was followed in which fresh marbles exhibit more intense TL emission in comparison with their archaeological counterparts (Figure 2).

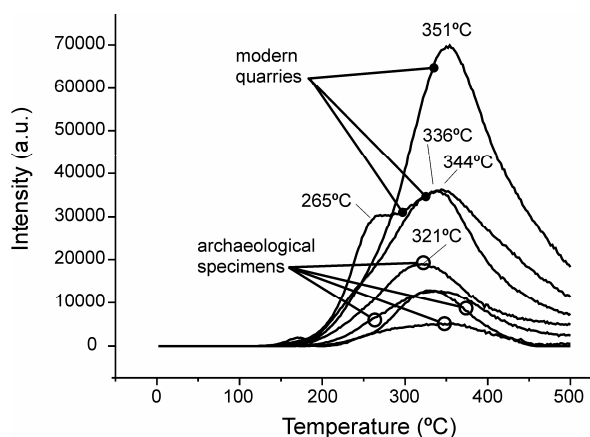


Fig. 2: Thermoluminescence glow curves of Aiani white marble specimens

The TL glow curves of as received aliquots of powdered marbles discriminate samples taken from modern quarries, exhibiting TL glow curves with larger intensity in comparison with their archaeological deteriorated counterparts. This general overview, supported on total intensities using broad spectra filters, arises as a simple methodology to authenticate disputable marble objects. All the TL curves display emission peaks circa 250°C as a shoulder encircled in maxima peak circa 350°C (Galloway, 2003; Polikreti et al., 2003).

Experiment 2.-

The CL analyses were performed in non-destructive mode to preserve both the Aiani archaeological and geological samples with

dissimilar results among them (Figure 3). All white marble samples from Aiani display the same CL spectrum shape; however they exhibit strong differences in the intensities of the blue (~330-480 nm) and red (~630 nm) CL bands showing CL emissions similar to both archaeological and geological samples.

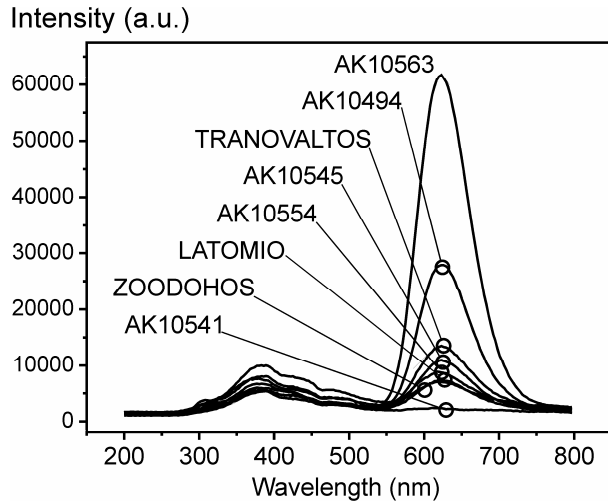


Fig. 3: CL spectra of Aiani archaeological white marbles (AK) and some modern geological samples (ZOODOHOS, LATOMIO, TRANOVALTO).

Hence, for comparison purposes these same spectra CL curves were redrawn in stock-pile mode including the total intensity (Figure 4). The total intensities such as the case of the 10,000 a.u. of sample ZOODOHOS involve comparable blue and red spectra bands intensities. A comparative looking to the CL spectra stockpile demonstrates the following features: (i) high total intensities involve a large red band and a relative low intensity in the blue region of the spectrum, e.g., case of the 70,000 a.u. of the sample AK10563, (ii) Low total intensities in the spectrum CL involve large blue bands in comparison with the red spectral region, e.g., 6,000 a.u. of the sample AK10541, (iii) Intermediate cases can be observed.

Experiment 3.-

The next experimental stage includes testing of the CL behaviour of a marble-cube subjected to temperatures changes. It was found that the CL of block of white marble reduces

asymmetrically from the core to the outer block after pre-annealing of 800°C / 3 hours.

The observed asymmetries of the cathodoluminescence emission intensity in the annealed block of Macael marble decrease from core to outer part of the block suggesting that the luminescent defects are better preserved at the near core of the marble block (Figure 5).

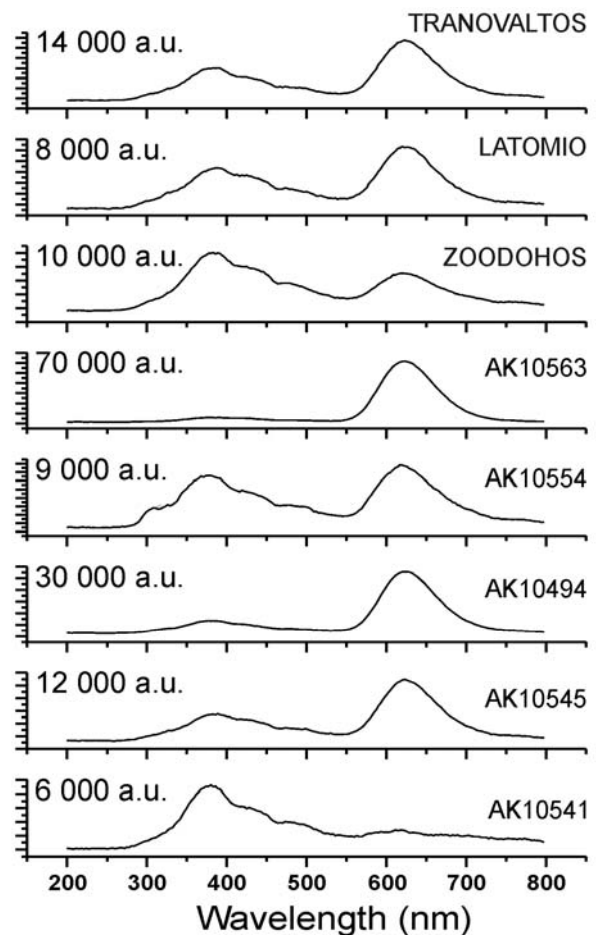


Fig. 4: Comparative stock-pile of the spectra CL analyses at room temperature of archaeological (AK) and geological (TRANOVALTOS, LATOMIO, ZOODOHOS) white marble specimens of Aiani (Greece).

Experiment 4.-

Finally, we perform ESEM-backscattering and CL-ESEM plots of natural fresh white marble pattern (figure 6) to enquire on the specific spatial contribution of each spectrum CL peak performing monochromatic plots on a little squared area sized 100x100 microns selected under the BSED probe of the ESEM microscope which also depicts a rhombohedra crystal of calcite (Figs. 6).

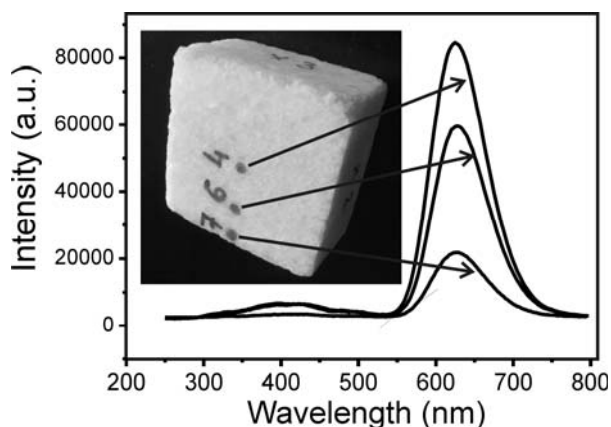


Fig. 5: The spectra CL emission intensity in an annealed block of marble gradually drops off from core to outer of the block.

The resulting CL spectrum exhibits a strong large peak at 627 nm characteristic of non-weathered marbles. This peak is attributed to Mn^{2+} luminescent centres in Ca^{2+} structural sites. In addition, the spectrum includes a complex emission band in the blue region with observable peaks at 330, 395, 425, 480 and 502 nm. This feature is due to the high resolution capability of the new MonoCL3 system attached to our FEI-ESEM microscope with a new parabolic mirror which can collect up to 75% of all light emitted from the marble using well-polished marble surfaces. The next step was to perform monochromatic CL maps of the selected area at 330, 395, 425, 480 and 502 nm (Figures 6).

A comprehensive examination of the CL results of figures 6 suggests the following data:

(i) the broad band of the blue region exhibit peaks which may be associated with different luminescence defects.

(ii) the 330 nm monochromatic mapping depicts a comparable image to the observed by the backscattering ESEM probe, highlighting the existent surfaces with remarkable clarity.

(iii) Conversely, the 395 nm monochromatic mapping depicts a CL image emitting much more CL from bulk rather than interfaces,

(iv) Furthermore, the 480 nm monochromatic mapping shows again more CL from interfaces rather than from bulk and

(v) the 627 nm monochromatic plot display a more luminous CL from the whole plot in

agreement with the 627 nm peak of the spectrum CL. In this case, clearly, the interfaces emit much more CL in comparison with the bulk.

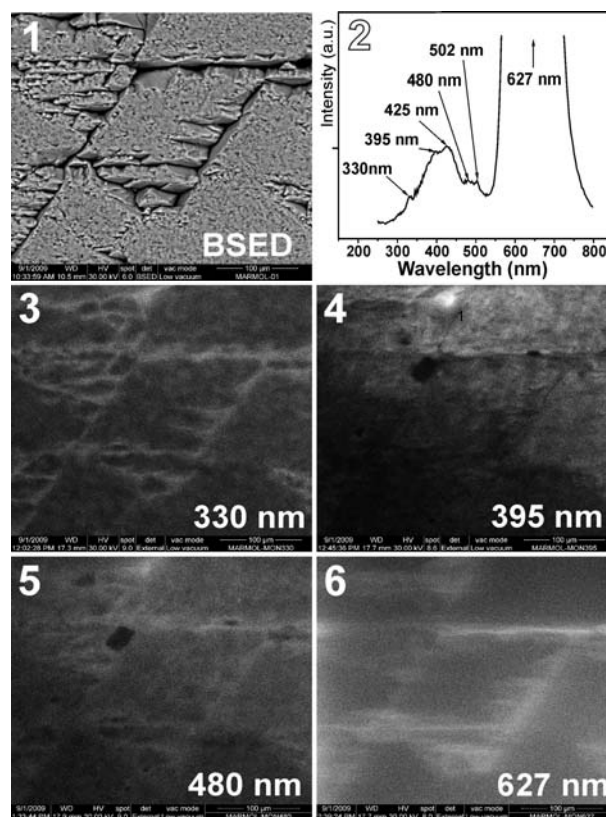


Fig. 6: Spectra CL under ESEM of white marble: (1) Backscattering image of a calcite crystal selection, (2) Spectrum CL, (3) Monochromatic plot at 330 nm, (4) Monochromatic plot at 395 nm, (5) Monochromatic plot at 480 nm, (6) Monochromatic plot at 627 nm.

DISCUSSION

TL emission measurements are commonly observed through a blue filter FIB002 of the Melles-Griot Company in which the wavelength is peaked at 320–480 nm. 320–480 nm, i.e., only the luminescence emission of broad blue band region of the spectrum is recorded. The TL glow curves of the examined samples are good enough to separate fresh marbles with intense TL emission from weathered marbles, exhibiting low TL emission. Beyond this observation it seems necessary to refine the marble spectra using a new high sensitivity MonoCL3 spectrometer under the electron microscope. Observing the stock-pile set of spectral CL of Aiani white marbles we infer that the blue band is more weathering resilient in comparison with

the red band which drops down easily under weathering. Conversely, the Mn^{2+} centres provide strong CL emission at circa 630 nm surrounded by a fresh and well-built calcite crystallographic lattice. In any case, the narrow cluster relationships among the spectra bands are evident since all possible common, or simple, emission defects and activators such as Mn^{2+} , Fe^{2+} , OH^- , H^+ , Mg^{2+} , are close interactions throughout the crystal bulk or bulk-interfaces, which must be considered as a "long-range system". We observe the 330 nm peak in other hydrothermal poly-grained carbonates from 320 to 340 nm such as the case of Smithsonite (Garcia-Guinea et al., 2009a) or Strontianite (Garcia-Guinea et al., 2009b). In these cases, the geological hydrothermal origin of the specimens' certify the intrinsic existence of hydroxyl groups in the interfaces which it is not the case of the metamorphic white marble needing weathering or wet burial. The experiment four detects that the spectra CL emission intensities drop off from the core to the outer of preheated which marble block (800°C / 3 hours).

During the geological recrystallization of the marble a self-assemblage of the calcite crystals set long distance correlations to reinforce a re-equilibration process producing twin's orientation disorder and other source of potential luminescence defects. Further annealing or wet burial modifies the whole stability of the marble fragment by self-organization in which the luminescence defects system is controlled not only by "short-range" but also by "long-range" elastic strain accommodation. Probably the most exciting results here included are depicted in the BSED and monochromatic plots (Figure 6), particularly the 330 nm monochromatic mapping depicting a comparable image to the one observed by the backscattering ESEM probe, highlighting the existent surfaces with remarkable clarity.

This datum could be interpreted as some type of luminescence emission-defect associated to defects of marble crystal interfaces, e.g., protons, hydroxyls, etc. Conversely, the 395 nm monochromatic mapping depicts a CL image emitting much more CL from bulk rather than interfaces; in this case we could better think on

"bulk defects", "point defects" or cationic activators in Ca^{2+} positions. Moreover the 480 nm monochromatic mapping shows again more CL emission from interfaces than from bulk with a similar way of thinking. The well-known red emission at 627 nm, i.e., Mn^{2+} defects in Ca^{2+} positions, exhibits a luminous monochromatic plot which is obvious in accordance with a maximum peak at 627 nm.

Furthermore, it is obvious that the interfaces are emitting more light in comparison with the crystal bulk. Accordingly, we must argue that those Mn^{2+} luminescent centres are not preferentially sited in the marble interfaces. Certainly, the 627 nm CL emissions are created inside bulk and some optical effect carry out photons from bulk to marble interfaces. Additional laboratory driven experimental must be conducted looking for responsible defects of the circa 330 nm CL emission associated to crystal surfaces since the 330 nm monochromatic mapping could also be explained by a bulk emission with photons travelling at the surface.

CONCLUSIONS

-- The TL emission measurements commonly observed through a blue filter at 320–480 nm merge together spectra peaks at 330, 395, 425 and 480 nm which show dissimilar spatial emission positions and must be associated to very different luminescence defects, in despite of the parallel behavior of the observed intensities under the physical changes, e.g., temperature, weathering.

--The experimental set of spectral CL curves of Aiani white marbles let us infer that the blue band is more weathering resilient in comparison with the red band which drops down easily under weathering. The Mn^{2+} centres provide strong CL emission at circa 630 nm surrounded by a well-built calcite crystallographic lattice.

-- The experimental comparison of spectra CL among Iceland calcite and white marble give a slight difference of the small 330 nm peak detected in marble which could be linked with defects sited in the grain interfaces of marble which are not observed in the "mono-crystal" pattern of Iceland calcite. We observe this same 330 nm

peak in other hydrothermal poly-grained carbonates with intrinsic hydroxyl groups in the interfaces which it is not the case of the metamorphic white marble needing weathering or wet burial to provide this 330 nm peak

-- The most exciting results here included are depicted in the BSED and monochromatic plots, particularly the 330 nm monochromatic mapping depicting a comparable image to the observed by the backscattering ESEM probe, high-

lighting the existent surfaces with remarkable clarity. This datum must be interpreted as some type of luminescence emission-defect associated to the marble crystal interfaces, e.g., protons, hydroxyls, etc.. Conversely, the 395 nm monochromatic mapping depicts a CL image emitting much more CL from bulk rather than interfaces; in this case we could better think on "bulk defects", "point defects" or cationic activators in Ca²⁺ positions.

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