# A combined petrographic and geochemical metrological approach to assess the provenance of the building limestone used in the Batalha Monastery (Portugal)

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Mosteiro da Batalha" [6], whereas their exact location was lost nowadays and was discovered by the authors. Field trips were made to these quarries (Fig. 2). 25 samples were collected, among which 13 samples were from Valinho do Rei and Pidiogo which were believed to be the original quarries for construction of monastery in 15th, 12 from the restoration quarries Reguengo do Fetal, Cabeço do Roxo and Outeiro de Sebastião. By special permission of the Direção-Geral do Patrimonio Cultural and the Mosteiro da Batalha authorities, 12 pieces of detached stone fragments were collected for destructive / non-destructive characterization respectively according to the protocol. The collected stone fragments came from various parts of the monastery, as labelled in Fig. 3.

*a* *b*

*Fig. 2. Photo records, latitude and longitude of a. Valinho do Rei (39°39'32.5"N 8°44'58.1"W) and b. Pidiogo (39°39'15.7"N 8°44'27.9"W) quarries*

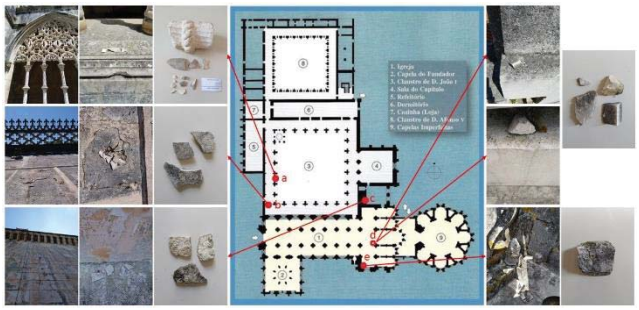


*Fig.3 Locations of samples collected from Batalha Monastery a. Royal cloister west gallery 3rd window outside (ground floor level) b. Royal cloister roof top (roof level) c. Church north aisle eaves arch (roof level) d. Church roof railing (roof level) e. Church south carved baluster (roof level)*

### *B. Thin section Petrography*

Thin sections of the stone samples were obtained using the following procedure: stones were cut into cuboid with a cross-sectional area of 2cm*3cm, the cross-sectional surface was polished by 220# sand paper, 400# and 1000# SiC powder with water sequentially. The polished stone surface was glued to the glass slide with epoxy resin and epoxy hardener mixed at the ratio of 2:0.9. After the epoxy glue consolidated, the stone were to 0.1~0.2 mm thickness, and polished using 400# and 1000# SiC powder with water till the thickness of the stone section reached 0.025mm. Thin sections were observed by Optical Microscopy using a LEICA DM2500P.

### *C. X-ray Diffraction (XRD)*

Stone samples were hand milled into powder in an agate mortar. The characterization was carried out using a X-ray diffractometer BRUKER D8 Discover, with a Cu Kα source and operating at 40 kV and 40 mA. Scans were run from 3 to 75 ° 2θ, with 0.05 2θ step and 1 s/step measuring time by point. Diffract-EVA software package (BRUKER/AXS GmbH, Germany) and the PDF-2 database files (ICDD, Denver, USA). software with PDF-2 mineralogical database was utilized to interpret XRD spectra. The semi-quantification was done using the Reference Intensity Ratio by Hubbard et al [7].

### *D. Thermal Gravimetric Analysis (TGA)*

The TGA analyses were conducted on a TG-DTA NETZSCH STA 449F3 Jupiter. The temperature of the sample was programmed at a heating rate of 10oC/min, increasing from 40ºC to 1000ºC, while the mass of the sample was monitored against time or temperature. For stone samples which contains absorbed or crystallized $H_2O$, carbonate minerals and hydroxide minerals, thermal decomposition with gaseous reaction can be tested.

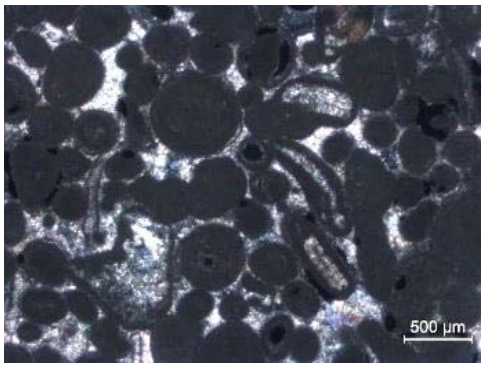
### *E. X-ray fluorescence (XRF)*

XRF analyses were performed operating a Benchtop EDXRF Bruker S2 PUMA using a methodology similar to that adopted by Georgiou et al [8]. Quantifications were obtained using a regression method with 19 standard reference materials [9]. Spectra Elements 2.0 was utilized for acquisition and data processing, reporting the final oxides/elements ($Na_2O$, MgO, $Al_2O_3$, $SiO_2$, $P_2O_5$, $SO_3$, $K_2O$, CaO, $TiO_2$, MnO, FeO) concentration and the instrumental statistical error. Two sample preparation methods were used: (1) 1.2g sample powder were fused with 12g flux (Li-tetraborate) on a Claisse LeNeo to form fused beads. (2) 10g sample powder were compressed with 1g wax (N,N'-dioctadecanoylethylenediamine) on a Specac Manual Hydraulic Press to form pellets.

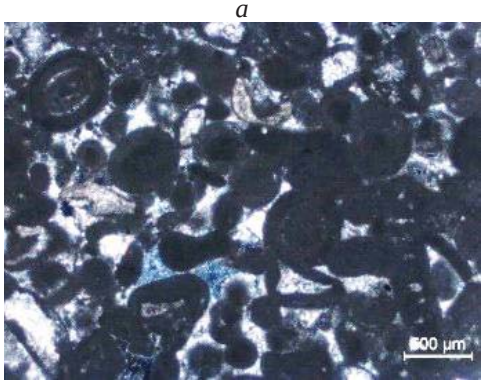
## III. RESULTS AND DISCUSSION

### *A. Thin section Petrography*

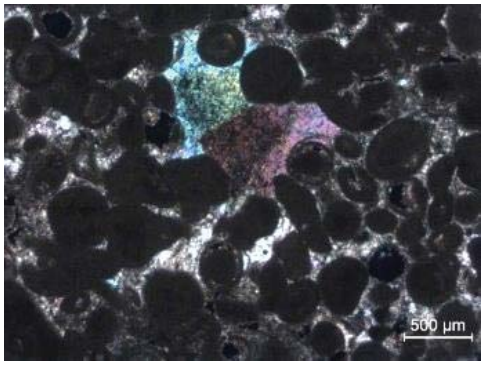
The microscope photos of thin-sections are presented in Fig. 4, on which the oolites, calcite crystals and fossils were clearly recognizable. According to the definition introduced by Flugel. Eof identifying paleontological fossils and classifying carbonate grains in microfacies studies, as well referring to previous biostratigraphy of carbonate succession by Cemile et al [10][11][12][13]. Table 2 summarizes the petrography features of the samples.



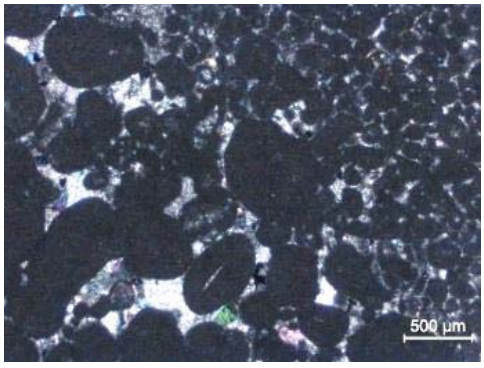

*a*




*b*




*c*




*d*

*Fig.4. Microscope photos of stone samples from a. Batalha Monastery, royal cloister; b. Batalha Monastery, church roof railing; c. Pidiogo quarry; d. Valinho do Rei quarry, lower layer.*

*Table 2. Petrographic and paleontological features of limestone thin sections.*

| Sample Name | Oolite size | Calcite Crystals | Grain Morphology | Fossils |
|---|---|---|---|---|
| Batalha Monastery, Royal Cloister | 150 ~ 500 µm | Micrite, Sparite | Peloids, Ooids, Aggregated grains; | Foraminifera, Gastropods |
| Batalha Monastery, roof top | 150 ~ 500 µm | Micrite, Sparite | Ooids, Oncoids | Foraminifera |
| Batalha Monastery, eaves arch | 200 ~ 400 µm | Micrite, Sparite | Ooids | Sponges |
| Batalha Monastery, church railing 1 | 200 ~ 500 µm | Micrite, Sparite | Peloids, Ooids | Sponges, Foraminifera, |
| Batalha Monastery, church railing 2 | 200 ~ 500 µm | Micrite, Sparite | Peloids, Ooids | Brachiopods |
| Batalha Monastery, baluster | 200 ~ 400 µm | Micrite, Sparite | Peloids, Ooids | Foraminifera, Wood |
| Pidiogo | 200 ~ 400 µm | Micrite, Sparite, | Peloids, Ooids | Gastropods, Ostracods, Intraclasts |
| Valinho do Rei, lower layer | 50 ~ 300 µm | Micrite, Sparite | Aggregated grains, Peloids, Ooids, Oncoids | Intraclasts, Brachiopods |
| Valihno do Rei, upper layer | 50 ~ 200 µm | Micrite, Sparite | Peloids; Aggregated grains | Foraminifera |

*B. X-ray diffraction*

The XRD results indicated that all the samples have the same mineral composition – calcite magnesian $\{(Mg_{0.064}Ca_{0.936})CO_3\}$ and quartz $\{SiO_2\}$. Fig. 5 shows the XRD scan of one sample from Pidiogo quarry. The semi-quantitative analysis provided the quality content of each mineral in the sample, as listed in Table 3. The proportion of calcite magnesian in these limestones has reached over 99%, while the content of quartz is lower than 1%.

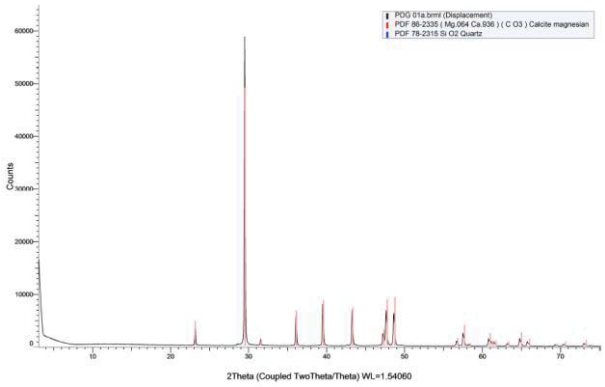



*Fig. 5. XRD of limestone taken from Pidiogo quarry.*

*Table 3. Semi-quantitative assessment of minerals in sample*

| Sample name | Calcite | Quartz |
|---|---|---|
| Batalha Monastery, Royal Cloister | 99.30% | 0.70% |
| Batalha Monastery, roof top | 99.41% | 0.59% |
| Batalha Monastery, eaves arch | 99.50% | 0.50% |
| Batalha Monastery, church railing 1 | 99.43% | 0.57% |
| Batalha Monastery, church railing 2 | 99.27% | 0.73% |
| Batalha Monastery, baluster | 99.40% | 0.60% |
| Pidiogo | 99.70% | 0.30% |
| Valinho do Rei, lower layer | 99.69% | 0.31% |
| Valihno do Rei, upper layer | 99.62% | 0.38% |

### *C. Thermal gravimetric analysis*

Fig. 6 shows the weight change of one sample according to temperature increase. A mass loss in the temperature range of 600 – 800 ºC was observed, indicating the decomposition reaction of calcite: $CaCO_3 \rightarrow CaO + CO_2$. The differential of thermal gravity curve showed the reaction is single-stepped. There is no mass change in other temperature range, demonstrating that there are no absorbed water, plaster, portlandite nor muscovite in these stones. Through the calculated results it is seen that calcite is the main composition of all the samples, the content reaches 97.2 wt% ~ 99.2 wt%.

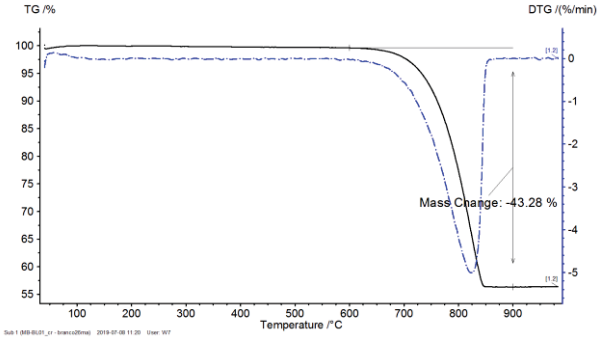



*Fig. 6. TGA curve of stone from Batalha Monastery, Baluster.*

### *D. X-ray fluorescence analysis*

Due to the same coordination number and similar ion radius that strontium and calcium cations have, the $Sr^{2+}$ may substitute a $Ca^{2+}$ ions in calcite. Stones formed in the same geological environment would have similar value of such substitution. From the Ca-Sr element alignment scatter plot, it is seen that the plot which represents Batalha Monastery baluster is very close to the plots of samples from the Valinho do Rei quarry, suggesting that the limestone of this baluster may come from the Valinho do Rei quarry. Similarly, the stone of Batalha Monastery eaves arch was suggested to be coming from the Pidiogo quarry.


*Fig. 7. Ca-Sr element alignment based on XRF.*

## IV. CONCLUSION

The proposed multi-analytical techniques were used for establishing the quarries of origin for the Batalha Monastery. Since considerable historical evidence can be drawn by the study of material provenance, these techniques have supplied a powerful tool to collect and analyze valuable information of special interest to conservation research.

The results of this work suggested that two parts of the monastery were constructed from the stones of Pidiogo quarry and Valinho do Rei quarry respectively. To verify the provenance of other parts of monastery, same analysis should be repeated on stones from the restoration quarries. In further research, ICP-MS is strongly advised to provide trace-element information in stones, for the confirmation of provenance.

## V. ACKNOWLEDGEMENT

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