Chemical and mineralogical analyses on stones from Sagunto Castle (Spain)

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For the first time, an archaeometric study was carried out on the carbonate rock ashlars of the Sagunto Castle. The studied site is one of the most important and best preserved Spanish archaeological and architectural monuments, characterized by different construction phases from the Roman period to Modern Ages. Forty samples collected from thirteen different structures of Sagunto Castle and two quarries, located in the Sagunto's hill were used for comparative purposes. The samples were analyzed by X-ray diffractions, X-ray fluorescence and inductively coupled plasma mass spectrometry to determine their mineralogical and elemental composition. The obtained data show similar chemical and mineralogical features between the rocks outcropping in the city quarrries and some of those employed to build the structures, suggesting that rocks could have been used to build the structures from different periods along the centuries.

1. Introduction

Chemical and mineralogical analyses of ancient stones have been used to identify raw material provenance and to better understand the constructive phases of both, archaeological sites (Ferrini et al., 2012; Columbu et al., 2014) and architectural monuments (Sammarco et al., 2015; Lezzerini et al., 2017), as well as to understand the exploitation and circulation of raw materials in the past (Dreesen and Dusar, 2004; Storemyr et al., 2007; Antonelli et al., 2014; Galle\textsuperscript{c}o et al., 2016). The analysis of the stones used for building ancient monuments could be also useful for conservation purposes, like getting specimens for laboratory tests, identifying replacement stone sources, and better understanding decay processes (Cardell et al., 2003; Brilli et al., 2010; Türök and Pi\kryl, 2010; De Kock et al., 2015; Hopkinson et al., 2015; Aali et al., 2016; Berthonneau et al., 2016; Lezzerini et al., 2016).

The present research aims to obtain the first chemical and mineralogical data of the stones used in the buildings of the Sagunto Castle, and to estimate their relationship with the stone material identified in the ancient quarries. Taking into account the difficult access to the amount of samples to be collected, allowed by the authorities, a chemical and mineralogical approach was developed on a set of forty building stone samples collected from thirteen different structures of the Castle (Fig. 1) and from two local quarries. Sagunto was inhabited by Iberian people before the V century BCE, but the expansion of the city and the construction of the most important structures started following the Roman conquest. The Sagunto Castle was characterized by several occupation phases since the Republican Roman period (Aranegui et al., 1987) to the Napoleonic Wars. During the past century, the site was also interested by restoration works and was designated as heritage of cultural interest by the public authorities (Ripollès Alegre and Llorens Forcada, 2004; Monserrat, 2007). Nowadays, this monument is preparing its candidature to be nominated UNESCO world heritage. The structures of the Sagunto Castle were built widely employing stones. The main used lithotypes are from the sedimentary sequences outcropping in the surrounding area of the site, and the Sagunto Castle itself is located on a hill where dolostone, marlstone and dolomitic limestone outcrop (Goy et al., 1972). Furthermore, the archaeologists identified two ancient quarries on the northern side of the hill. In this study, X-ray diffraction (XRD) was used to determine the main mineralogical phases of the samples, while X-ray fluorescence...
(XRF) and inductively coupled plasma mass spectrometry (ICP-MS) were employed to determine major and minor chemical elements and trace chemical elements, respectively. The obtained data were processed by multivariate statistics.

The importance behind this research is related to the high cultural significance of the Sagunto Castle archaeological site and the unique possibility to produce significant data, which was quite difficult due to the high protective policy that restricts the access to building stone and outcrop sampling.

2. Materials and methods

2.1. Sampling

Forty stone samples were collected from different structures of the Sagunto Castle. They are representative of the different chronological phases identified during the archaeological studies (Table 1). Due to conservation issues, we were allowed by the authorities to collect just around 1 g of each sample in order to perform the analysis, limiting the range of analytical methods to be performed. A small surface portion of each ashlar was scraped to remove the external surface, in order to avoid weathered material, and small chips of rock were then collected by using a chisel.

Twenty-two samples were collected from buildings whose foundation was dated to the Roman Republican period (Roman Republican wall, RW; Diana Temple, DT; Republican Forum, RF; Central Estudiantes Tower, TC). However, concerning TC, the archaeological evidence and mortars analysis (Gallello et al., 2017) suggest important reworks in the subsequent phases.

The Roman Imperial phase led to the building of important monumental structure such as the Theatre (TR), from which two samples were collected. Moreover, five samples were collected from the Imperial Forum (Curia, FC; Basilica, FB; Tabernae, FT), an area affected by reworks during the Islamic phase.

As indicative of the Islamic period, begun in the VIII century and endured with reversal of fate until the reconquest of the XIII century, four samples were collected from different buildings (Islamic Gate, IG; Islamic Wall, IW; Moneda Tower, MT). Three samples were also collected from Modern Age buildings (Hermitage, HR; Modern Wall, MW; Napoleonic Barracks, NB).

In order to evaluate the possible relationship between construction building stones and local outcropping sedimentary rocks, four representative samples of the two ancient quarries on the hill of the Sagunto Castle located at Calvario (CQ – Calvario Quarry) and at the Theatre (TQ – Theatre Quarry) areas, were taken. These quarries are formed by dolostone and dolomitic limestone of Triassic “Muschelkalk” outcrop (Goy et al., 1972).

2.2. Methods

We have designed an analytical method approach in order to provide reproducible and comparable results compatible with the small amount of available sample. Qualitative mineralogical analyses were carried out on powders through X-ray diffraction (XRD) by using an automatic diffractometer Philips PW 1830/1710 under the following experimental conditions: Bragg-Brentano geometry, Ni-filtered CuKα radiation obtained at 40 kV and 20 mA, 5–60°2θ investigated range in step of 0.02° with a counting time per step of 2 s. To identify the mineralogical phases in the X-ray spectra, a search/match approach (DIFFRACPlus EVA) was used by comparing experimental peaks with PDF2 reference patterns.

Major and minor chemical elements were determined by X-ray fluorescence (XRF) on fused glass disks utilizing an ARL 9400 XP+ sequential X-ray spectrometer under the instrumental conditions reported by Lezzerini et al. (2013). Within the range of the measured concentrations, the analytical uncertainties determined on international standards vary from 20% (Na2O) to 1% relative (CaO), with a mean value of 5% relative for the major elements (Lezzerini et al.,...
The obtained solutions were cautiously transferred into plastic sample vials, while placing them in a water bath at 100 °C for 40 min. The solutions were analyzed with a Perkin Elmer Elan DRCII ICP-MS (Concord, Ontario, Canada). Digested samples were run through multivariate statistics. Specifically, Principal Component Analysis (PCA) was carried out employing 40 samples and 21 variables (Na2O, MgO, CaO, MnO, Fe2O3, REE, Y and Sc). This statistic method was used to explore large geochemical data-sets reducing the number of variables and providing a deep insight into the structure of their variance. Data were pre-processed through mean centering and autoscaling. Venetian blind cross validation was carried out to test the prediction capability of the built model. The PLS Toolbox 8.2 for Eigenvector Research Inc. (Wenatchee, WA, USA) running in the software Matlab R2016b from Mathworks Inc. (Natick, MA, USA) was used for statistical treatments.

### 3. Results and discussion

#### 3.1. Mineralogical composition

The collected XRD spectra (Table 2) revealed that calcite and dolomite are the main mineralogical phases in the studied samples. So, looking at calcite and dolomite relative amounts, the presence of almost three different lithotypes could be estimated:

- Group 1: limestones characterized by the presence of calcite and traces of dolomite (19 samples: RW1-6, RW8, TC1, DT1, RF1, FC1-2, FB1, FT1, TR2-3, IG1-2, MW1);
- Group 2: calcitic dolostones characterized by high contents of dolomite and traces or small amounts of calcite (10 samples: TC4, TC5, TC8-9, RF2, IW1, HR1, NB1, TQ1-2);
- Group 3: stones characterized by high amount of calcite and dolomite, even with different relative proportion (11 samples: RW7, TC2-3, TC5, TC7, DT2, RF3, FT2, MT1, CQ1-2).

Additionally, minor contents of quartz were detected in each sample and a small amount offeldspars was found in samples of the second and third group. Furthermore, traces of phyllosilicates in sample RF2 and a small amount of feldspars was found in samples of the second and third group. Additionally, traces of phyllosilicates in sample RF2 and a small amount of gypsum in the samples from the Islamic Gate (IG1-2) were detected. In limestone gypsum is a typical secondary mineral in limestone that can be produced by the reaction of calcite and sulfurous acid due to environmental chemical alterations as air pollution (Charola et al., 2007). However it is difficult to understand if the presence of this mineral is due to the conservation state of the masonries, since it was detected only in the Islamic Gate samples.

#### 3.2. Major and minor elements

Chemical XRF data reported in Table 2 indicates that MgO and CaO are the most representative components of the analyzed samples showing a strong negative correlation (Fig. 2a). These results confirm those obtained by mineralogical analyses, in fact according to Frolova classification of calcite-dolomite series (Frolova, 1959), CaO/MgO ratio can be used to discriminate between calcite- and dolomite-rich carbonate rocks. Based on the aforementioned classification criterion, the CaO/MgO ratio was calculated in order to verify discriminations inferred by mineralogical composition, and better define the geological nature of rock samples in which both calcite and dolomite were identified.

Samples of Group 1 exhibit a CaO/MgO ratio > 50.1, confirming the previous classification as limestones; samples of Group 2, identified as calcitic dolostones by XRD data, can be precisely defined as slightly calcitic dolostones, being characterized by a CaO/MgO ratios ranging from 1.8 to 2.0. For all the other samples, the calculated CaO/MgO ratios allow us to discriminate calcitic dolostones (CaO/MgO ratios from 2.3 to 3.3: TC5, DT2, RF3, FT2 and CQ1), dolomitic limestones (CaO/MgO ratios of 4.2, RW7, and 8.3, CQ2), and slightly dolomitic.
Concerning the significance of other major elements, usually iron and manganese oxides are directly correlated to the presence of dolomite (Morrow, 1982); effectively, while in samples characterized by medium and high amounts of this mineral Fe$_2$O$_3T$ ranges from 0.82 to 4.31 wt% (mean: 2.21 ± 0.48 wt%), in limestones Fe$_2$O$_3T$ ranges from 0.20 to 1.03 wt% (mean: 0.52 ± 0.19 wt%) and MnO from 0.01 to 0.02 wt% (mean: 0.012 ± 0.004 wt%). The compositional differences among the possible sedimentary rocks types identified on the basis of CaO/MgO ratio are also evident by trends shown in the binary diagrams reported in Fig. 2b and c.

Concerning elements useful to inspect the conservation state of building materials and, the possible degradation processes of structures, it is noteworthy that IG1 and IG2 show contents of Na$_2$O one order of magnitude higher than in the other samples: namely 0.21 and 0.17 wt%, respectively. Such a high amount of sodium could be related to the presence of soluble salts responsible for severe decay in buildings (Charola et al., 2007). On the contrary, the low amount of sodium in dolomitic limestones and dolostones, as compared to limestones, could be explained by the diagenesis process of these rocks (Abdel-Rahman and Nader, 2002). On the other hand, it must be noticed that TQ1 is characterized by a high content of SiO$_2$ (6.46%), although the highest value was detected in sample RW2 (11.55%), while the stones collected from TQ quarry show high amounts of TiO$_2$ (TQ1: 0.16% and TQ2: 0.13%).

### 3.3. Trace elements analysis

Table 3 shows the results of trace element analysis performed through ICP-MS, expressed in μg/g. Regarding the total amount of REE (2REEE), all the samples contained from 1.2 to 28 μg/g, except limestone samples RW2, MW1 and TR2, which have anomalous high concentrations of lanthanides: 84, 100 and 114 μg/g, respectively. These samples have also high amounts of yttrium (RW2: 9.6 ± 2.8 μg/g), while the others contain this element from 0.2 to 3 μg/g. Scandium vary from 0.6 to 16 μg/g. In general, the limestone samples (29 ± 23 μg/g) show averagely higher 2REEE values than the ashes of the other carbonate rocks (12 ± 6 μg/g) and the quarry samples (6 ± 2 μg/g), also excluding the above-quoted anomalous values. The limestone samples are also characterized by high amounts of strontium ranging from 78 to 3003 μg/g (796 ± 781 μg/g) while the other samples range between 46 and 1211 μg/g for ashes (184 ± 306 μg/g), and between 37 and 112 μg/g for quarry rock (66 ± 35 μg/g). On the other hand, Cr and Li are higher in dolomite limestone and dolostone quarries (50 ± 28 μg/g and 1.8 ± 0.8 μg/g), than in limestone ones.
The chemical and mineralogical results of stones sampled from Sagunto Castle, are showing the five different facies of dolostone and limestone lithologies (calcitic dolostones, slightly calcitic dolostones, dolomitic limestones, slightly dolomitic limestones and limestones) all of them outcropping in the sedimentary sequence of the Sagunto area as indicated by Goy et al. (1972). This discrimination, suggested by chemical and mineralogical data, has been confirmed by the relative amounts of CaO and MgO (Fig. 2) and by the variability in minor and trace elements (Fig. 3).

Concerning provenance issues, the first test seems to indicate a compositional semblance between dolomite-rich ashlars (slightly calcitic dolostone, calcitic dolostone, dolomitic limestone, and slightly dolomitic limestone) and stone samples from local quarries. Furthermore, the representative samples taken from the ancient quarries show a slightly different mineralogical composition, covering the whole range of carbonate rocks: the stones from Theatre Quarry may be classified as slightly calcitic dolostones, while the Calvario Quarry materials may span from calcitic dolostone to dolomitic limestone. In fact, the fortress of Sagunto Castle is built on the rock outcrop of Triassic “Muschelkalk” lithologies, which show different intermediate facies from dolostone to dolomitic limestone. The lithotypes sampled from the Sagunto Castle structures maybe indicate that the stones employed could be from those local quarries. Regarding limestones, until now no local ancient quarries have been identified in the closeness of Sagunto, although the area is interested by the occurrence of this lithotype just few kilometers south-west and north-west of the archaeological site. In this latter area, some Triassic “Buntsandstein” limestones of Liás (Pliensbachien, Sinemuriense, Hettangiense) also appear, together with dolomites, bioclastic-limestones and carniolas. Within a radius of 5 km from the Castle various limestone facies of Dogger and Lower Malm (Oxfordiense) and marly limestones with nodules were also identified (Goy et al., 1972).

If we try to find a relation between the different lithotypes and the construction phases of the Castle, it can be observed that limestones have been employed in all Imperial buildings (i.e.: Curia, Basilica and Theatre, with the exception of FT2 sample), in the Islamic Gate and in the Modern Wall. Limestone ashlars occur with a non-systematic
distribution in some Republican structures, such as the Republican Forum (RF1), Diana Temple (DT1) and the Central Estudiantes Tower (TC1). It is worth noticing that the Republican wall seems to be entirely constructed by using this lithotype (samples labeled as RW), with the sole exception of RW7, which shows an a distribution in some Republican structures, such as the Republican Forum (RF1), Diana Temple (DT1) and the Central Estudiantes Tower (TC1). It is worth noticing that the Republican wall seems to be entirely constructed by using this lithotype (samples labeled as RW), with the sole exception of RW7, which shows an affinities with the Calvario Quarry materials (specifically, CQ2 sample). In the other studied structures, materials were possibly taken from Calvario and Theatre quarries. Trace analyses (Gallello et al., 2017), seems to point out the presence of at least two construction phases during this period or the presence of some architectural intervention on these structures during the following periods. However, it is worth noting that dolomite-rich rocks were used in buildings whose mortars evidenced Islamic (TCE, FT, HR, IW and TM) and Modern (TCE, NP) construction phases (Gallello et al., 2017; Ramacciotti et al., 2018), suggesting a possible heavy exploitation of the city quarries during Medieval and Modern Ages. In conclusion, the occurrence of all the identified stone types in the overall archaeological area supports the considerations, suggested by the previous archaeological and archaeometric studies on Sagunto Castle mortars (Gallello et al., 2017), according to which heavy reworks interested most of the buildings from the Roman period to the Modern Ages.

4. Conclusions

This study have demonstrated the capability of chemical and mineral analyses in discriminating carbonate rocks and supporting archaeological studies, providing information on raw materials provenance and reconstruction of architectural phases, also when just a small amount of sample can be collected.

The results suggest that the dolomitic rock facies (mainly calcitic dolostones and dolomitic limestones) used to erect the Sagunto Castle maybe come from the local “Theatre” and “Calvario” quarries. Trace elements, REE, Y and Sr showed to be good discriminators of these
rocks from the others. The lower variability in these elements enforces the above-quoted provenance hypothesis of dolomitic limestones and dolostones.

Regarding the limestone facies, although no extraction front or ancient quarry have been recognized near to the archaeological site, it is likely that these stones come from the outcrops located next to the castle (within about 2 km), where lithologies similar to those used in the castle were found. No conclusions can be inferred by the higher variability of both lanthanides, yttrium and Sr in limestone ashlars due to the impossibility of identifying the ancient quarries and determining the variability of the possible raw materials. However, REE and Y point out the presence of three limestone samples characterized by abnormally high values (RW2, MW1 and TR2).

The results suggest the presence of different construction phases in
RW, RF and FT during the Republican period. Limestone from the unidentified quarries outside the city could have been preferentially used during the Roman Ages, while calcitic dolostone and dolomitic limestone possibly extracted from the urban quarries seems to be especially exploited during the Islamic period and Modern Ages, as suggested by their preferential employment in buildings like TCE, FT, HR, IW, TM and NP.

This study provides a unique opportunity to chemically screen this important site, which is being considered as a candidate to be declared a UNESCO world heritage. The unsystematic occurrence of the different identified lithotypes in the studied buildings enforces the idea of a complex architectural history of the Sagunto Castle, characterized by reworks and whose complete understanding is probably only at its starting point.

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