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

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ABSTRACT

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 diffraction, 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 quarries 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; Gallello 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; Török and Přikryl, 2010; De Kock et al., 2015; Hopkinson et al., 2015; Aalil 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 (Ripollés 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

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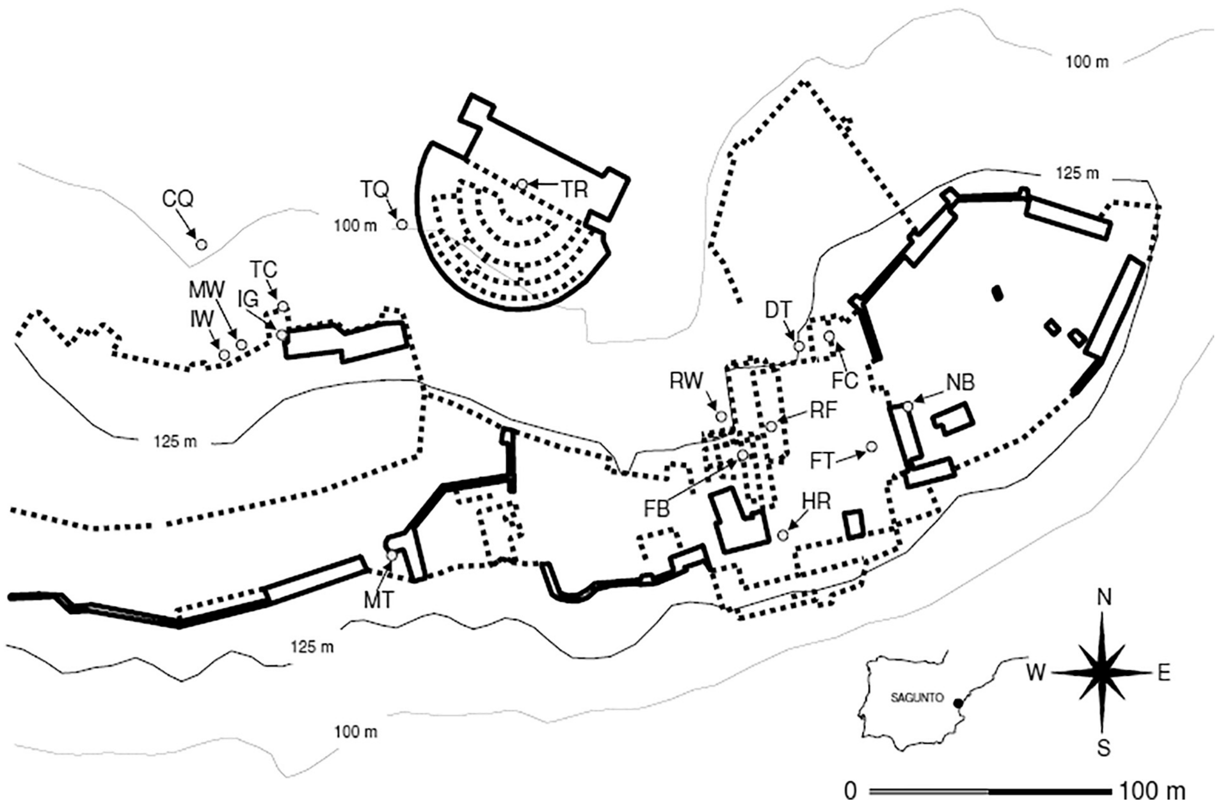

Fig. 1. Map of Sagunto Castle with sampling points (modified from Gallello et al., 2017).

(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 CuK_{α} 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% (Na_2O) to 1% relative (CaO), with a mean value of 5% relative for the major elements (Lezzerini et al.,

Table 1
List and identification of collected samples.

Sample	Building	Period	Sample	Building/quarry	Period
RW1	Republican wall	Roman Republican	RF2	Republican forum	Roman Republican
RW2	Republican wall		RF3	Republican forum	
RW3	Republican wall		FC1	Imperial forum Curia	Roman imperial
RW4	Republican wall		FC2	Imperial forum Curia	
RW5	Republican wall		FB1	Imperial forum basilica	
RW6	Republican wall		FT1	Imperial forum tabernae	
RW7	Republican wall		FT2	Imperial forum tabernae	
RW8	Republican wall		TR2	Theatre	
TC1	Torre central estudiantes		TR3	Theatre	
TC2	Torre central estudiantes		IG1	Islamic gate	Islamic period
TC3	Torre central estudiantes		IG2	Islamic gate	
TC4	Torre central estudiantes		IW1	Islamic wall	
TC5	Torre central estudiantes		MT1	Moneda tower	
TC6	Torre central estudiantes		HR1	Hermitage	Modern ages
TC7	Torre central estudiantes		MW1	Modern wall	
TC8	Torre central estudiantes		NB1	Napoleonic barrack	
TC9	Torre central estudiantes		CQ1	Calvario quarry	–
DT1	Republican Diana temple		CQ2	Calvario quarry	–
DT2	Republican Diana temple		TQ1	Theatre quarry	–
RF1	Republican forum		TQ2	Theatre quarry	–

2013; Lezzerini et al., 2014). The total amount of volatile components was determined as loss on ignition (LOI) in 105–950 °C temperature range.

Trace elements (Ba, Bi, Cd, Cr, Co, Cu, Pb, Li, Mn, Mo, Ni, Sr, Tl, V, Zn), REE (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), Sc and Y were determined by ICP-MS. The dissolution of homogenized samples was carried out by adding 1.35 ml of hydrochloric acid and 0.45 ml of nitric acid (using high purity 37% HCl and 69% HNO_3) to 0.15 g of sample in glass tubes, while placing them in a water bath at 100 °C for 40 min. The obtained solutions were cautiously transferred into plastic tubes of 50 ml and diluted up to 15 ml with purified water. The calibration standards were prepared from a stock solution for ICP analysis in HNO_3 5% (w/v), containing the mentioned elements at a concentration of 100 μg/ml. Solutions were analyzed with a Perkin Elmer Elan DRCII ICP-MS (Concord, Ontario, Canada). Digested Samples were filtered employing filter paper (Whatman™N.1, 70 mm) to eliminate the insoluble residue and to avoid the obstruction of the nebulization system. Concentrations between 1 and 600 μg/l were used for calibration purpose of most of the elements (Ba, Bi, Cd, Cr, Co, Cu, Pb, Li, Mn, Mo, Ni, Sr, Tl, V, Zn, La, Ce, Pr, Nd), and concentrations between 1 and 100 μg/l for Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu. All standards were purchased from Sharlab S.L. (Barcelona). Soil JDo-1 and limestone NCS DC73375 certified materials were used to control the quality of measurements. Rhodium was used as internal standard.

Selected major and trace elements data obtained on studied stone samples were processed through multivariate statistics. Specifically, Principal Component Analysis (PCA) was carried out employing 40 samples and 21 variables (Na_2O, MgO, CaO, MnO, Fe_2O_3T, REE, Y and Sc). This statistic method was used to explore large geochemical datasets 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 as the way 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 MatlabR2016b 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, TC6, 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 of feldspars was found in samples of the second and third group. Furthermore, traces of phyllosilicates in sample RF2 and small amount of gypsum in the samples from the Islamic Gate (IG1-2) were found. In limestone gypsum is a typical secondary mineral in limestone that can be produced by the reaction of calcite and sulfuric 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

Table 2
Main mineralogical phases of Sagunto Castle samples and estimated amounts of oxides determined by XRF, XRD, and their volatile components (LOI).

Sample	Cal	Dol	Qtz	Fsp	Other	L.O.I.	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3 T	CaO/MgO	Classification
RW1	XXX	tr	X	–	–	42.8	0.02	0.95	0.43	1.69	0.08	0.28	53.2	0.03	0.01	0.47	56.0	Ls.
RW2	XXX	–	X	–	–	38.4	0.03	0.57	0.71	11.6	0.09	0.27	48.1	0.02	0.01	0.31	84.4	Ls.
RW3	XXX	–	X	–	–	41.5	0.03	0.86	1.26	3.25	0.13	0.69	51.7	0.06	0.01	0.56	60.1	Ls.
RW4	XXX	–	X	–	–	42.1	0.05	0.54	0.89	2.37	0.08	0.49	52.9	0.05	0.01	0.46	98.0	Ls.
RW5	XXX	–	X	–	–	43.1	0.02	0.57	0.31	1.14	0.07	0.20	54.2	0.02	0.01	0.37	95.0	Ls.
RW6	XXX	–	X	–	–	42.8	0.02	0.55	0.47	1.45	0.14	0.26	53.7	0.02	0.02	0.52	97.7	Ls.
RW7	XX	XXX	X	X	–	43.4	0.01	5.73	0.49	1.71	0.09	0.27	47.4	0.04	0.05	0.82	8.3	Dolomitic ls.
RW8	XXX	–	X	–	–	43.1	0.02	0.63	0.36	1.03	0.08	0.24	54.1	0.02	0.01	0.45	85.8	Ls.
TC1	XXX	tr	X	–	–	42.7	0.02	1.01	0.55	1.79	0.15	0.38	53.0	0.04	0.01	0.44	52.4	Ls.
TC2	XXX	X	X	–	–	42.1	0.02	2.55	1.12	2.54	0.11	0.72	50.1	0.07	0.02	0.73	19.6	Slightly dolomitic ls.
TC3	XXX	X	X	–	–	42.1	0.03	2.15	0.98	2.44	0.15	0.64	50.7	0.06	0.01	0.70	23.6	Slightly dolomitic ls.
TC4	tr	XXX	X	X	–	43.6	< LOD	16.7	1.25	2.81	0.14	0.61	32.3	0.07	0.13	2.34	1.9	Slightly calcitic dls.
TC5	XX	XXX	X	X	–	42.4	0.02	12.9	1.87	3.52	0.12	0.92	36.0	0.12	0.10	2.01	2.8	Calcitic dls.
TC6	tr	XXX	X	X	–	43.6	0.01	16.7	1.20	2.52	0.17	0.58	32.3	0.09	0.10	2.74	1.9	Slightly calcitic dls.
TC7	XXX	XX	X	–	–	41.8	0.04	4.40	1.16	2.67	0.08	0.56	47.1	0.08	0.08	2.00	10.7	Slightly dolomitic ls.
TC8	tr	XXX	X	X	–	44.9	< LOD	16.9	0.47	1.88	0.10	0.23	33.8	0.03	0.04	1.66	2.0	Slightly calcitic dls.
TC9	tr	XXX	X	X	–	44.7	0.02	17.1	0.60	1.82	0.11	0.24	33.3	0.03	0.14	1.96	1.9	Slightly calcitic dls.
DT1	XXX	–	X	–	–	42.2	0.03	0.88	0.83	2.38	0.08	0.52	52.5	0.04	0.01	0.51	59.7	Ls.
DT2	XX	XXX	X	X	–	45.1	< LOD	15.4	0.39	1.32	0.10	0.17	36.0	0.02	0.06	1.38	2.3	Calcitic dls.
RF1	XXX	tr	X	–	–	42.8	0.04	0.78	0.44	1.37	0.07	0.26	53.5	0.02	0.01	0.64	68.6	Ls.
RF2	tr	XXX	X	X	Phyll (tr)	44.0	0.02	17.0	0.90	2.40	0.19	0.41	32.4	0.06	0.13	2.43	1.9	Slightly calcitic dls.
RF3	XX	XXX	X	X	–	44.4	0.02	12.5	0.62	1.23	0.22	0.25	39.3	0.04	0.07	1.34	3.1	Calcitic dls.
FC1	XXX	–	X	–	–	43.0	0.04	0.61	0.42	1.15	0.06	0.24	53.9	0.02	0.01	0.52	88.4	Ls.
FC2	XXX	tr	X	–	–	42.6	0.04	0.76	0.55	2.09	0.07	0.32	53.2	0.03	0.01	0.36	70.0	Ls.
FB1	XXX	–	X	–	–	41.9	0.03	0.79	1.08	2.62	0.08	0.63	52.3	0.05	0.01	0.60	66.1	Ls.
FT1	XXX	tr	X	–	–	42.5	0.03	0.91	0.61	1.80	0.08	0.35	52.8	0.03	0.02	0.86	58.1	Ls.
FT2	XX	XXX	X	X	–	44.23	0.02	14.99	0.54	2.2	0.07	0.25	35.51	0.03	0.13	2.03	2.4	Calcitic dls.
TR2	XXX	–	X	–	–	43.4	0.02	0.82	0.25	0.77	0.10	0.13	54.1	0.02	0.01	0.37	66.0	Ls.
TR3	XXX	–	X	–	–	41.9	0.04	0.77	1.02	2.62	0.10	0.66	52.3	0.06	0.02	0.56	67.9	Ls.
IG1	XXX	–	X	–	Gp (X)	43.1	0.21	0.59	0.31	1.01	0.11	0.34	54.1	0.02	0.01	0.25	91.6	Ls.
IG2	XXX	–	X	–	Gp (X)	43.2	0.17	0.49	0.27	0.76	0.32	0.26	54.3	0.01	0.01	0.20	110.9	Ls.
IW1	tr	XXX	X	X	–	45.1	0.02	17.4	0.59	1.32	0.13	0.26	33.3	0.03	0.11	1.72	1.9	Slightly calcitic dls.
MT1	XXX	X	X	–	–	42.5	0.06	1.84	0.72	2.17	0.08	0.49	51.6	0.03	0.01	0.49	28.0	Slightly dolomitic ls.
HR1	tr	XXX	X	X	–	43.5	0.04	17.5	1.25	3.31	0.08	0.58	31.1	0.08	0.15	2.37	1.8	Slightly calcitic dls.
MW1	XXX	–	X	–	–	41.8	0.08	0.51	0.84	2.57	0.24	0.33	52.6	0.05	0.02	1.03	103.0	Ls.
NB1	tr	XXX	X	X	–	43.8	< LOD	16.6	1.30	2.59	0.10	0.67	32.8	0.08	0.14	1.94	2.0	Slightly calcitic dls.
CQ1	XX	XXX	X	X	–	44.1	< LOD	12.0	0.65	1.58	0.08	0.31	39.5	0.04	0.04	1.69	3.3	Calcitic dls.
CQ2	XX	XXX	X	X	–	43.8	< LOD	9.92	0.57	1.55	0.08	0.27	42.1	0.03	0.03	1.63	4.2	Dolomitic ls.
TQ1	tr	XXX	X	X	–	40.9	0.02	16.2	2.84	6.46	0.14	1.16	29.6	0.16	0.13	2.34	1.8	Slightly calcitic dls.
TQ2	tr	XXX	X	X	–	43.1	0.01	17.2	1.86	3.84	0.08	0.80	31.1	0.13	0.09	1.83	1.8	Slightly calcitic dls.

Minerals and rocks acronyms: Cal = calcite, Dol = dolomite, Qtz = quartz, Fsp = feldspars, Phyll = phyllosilicates, Gp = gypsum, Ls. = limestone, Dls. = dolostone. XXX = large amounts, XX = medium amounts, X = small amounts, tr = trace, − = not detected. The amount of chemical elements is expressed in weight percentage. L.O.I. = loss on ignition (950 °C); Fe_2O_3 T = total iron expressed as Fe_2O_3; < LOD = under the limit of detection.

limestones (CaO/MgO ratios from 10.7 to 28.0: TC2, TC3, TC7, and MT1).

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_2O_3T ranges from 0.82 to 2.74 wt% (mean: 1.90 ± 0.46 wt%) and MnO from 0.03 to 0.15 wt% (mean: 0.10 ± 0.04%), in limestones Fe_2O_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 evidenced 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_2O 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 (ΣREE), 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 μg/g, MW: 29 μg/g and TR2: 22 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 ΣREE values than the ashlars 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 ashlars (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 samples, both from buildings (39 ± 50 μg/g and 1.4 ± 0.9 μg/g) and quarries (50 ± 28 μg/g and 1.8 ± 0.8 μg/g), than in limestone ones

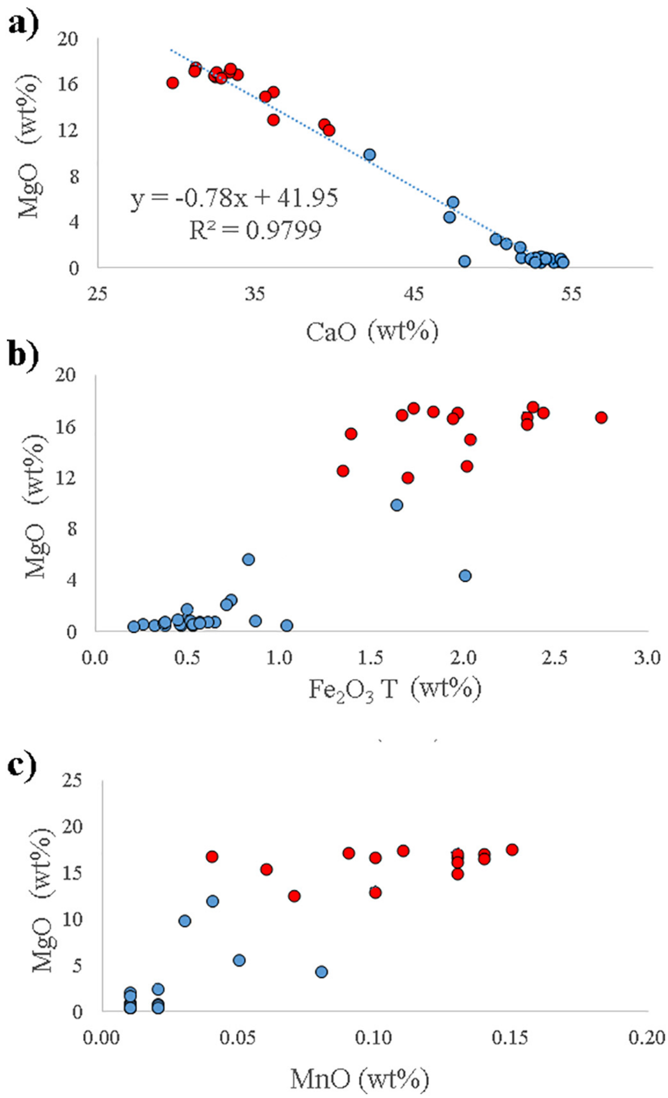

Fig. 2. Binary diagrams (a) CaO vs. MgO; (b) Fe2O3T vs. MgO; (c) MnO vs. MgO. Legenda: red circles = calcitic dolostone; blue circles = limestone and dolomitic limestone.

(16 ± 22 μg/g and 0.9 ± 0.7 μg/g). Furthermore, dolomite limestone-dolostone ashlars and quarry samples have higher levels of Zn (31 ± 28 μg/g and 51 ± 46 μg/g respectively) than limestone ones (21 ± 22 μg/g), and the first ones have higher concentrations of Pb (22 ± 17 μg/g) than limestone and quarry samples (13 ± 12 μg/g and 14 ± 13 μg/g respectively). Other trace elements were found in comparable concentrations in the three types of samples.

3.4. Statistical data processing

Multivariate statistics was carried out to evaluate the similarities and differences among the analyzed samples by applying PCA. In order to reduce the number of variables which could describe appropriately the samples, Na_2O, MgO, CaO, MnO, Fe_2O_3T, REE, Y and Sc of the whole set of samples were used (Fig. 3) due to the important role of these elements on the sedimentary rock composition (Schieber, 1988; Nothdurft et al., 2004; Zhang et al., 2017).

Just two principal components (PC1 and PC2) explain 58.04% and 17.98% of the variance, respectively, and loadings of PC1 and PC2 are correlated with their contribution to the overall model (Fig. 3, bottom). REE data especially contribute on PC1 direction, while PC2 is particularly influenced by major elements (Fig. 3, bottom). Specifically, PC1 accounts La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu and Y variability and higher values of REE mean higher values of PC1. Otherwise, the influence of Na_2O, MgO, CaO, MnO and Fe_2O_3T in discriminating different lithotypes is evidenced by PC2 scores; as can be seen, Na_2O and CaO, and MgO, MnO and Fe_2O_3T inversely contribute to the computation of PC2, meaning that higher values of the first elements, typical of limestone, lead to negative values on y-axis and higher values of the latter ones, typical of magnesian carbonate rocks, lead to positive ones.

The inspection of scores plot shown in the top of Fig. 3 allows to discriminate two main sample populations: in PC2 positive direction, samples exhibiting the presence of dolomite, classified from slightly dolomitic limestones (TC7 and RW7) to calcitic dolostones, are grouped together with the samples taken from both studied local quarries (labeled as TQ and CQ). Conversely, limestone ashlars and most of the slightly dolomitic limestones are grouped on the bottom of the plot. It is noteworthy that dolomitic stones seem to exhibit a more homogenous composition than limestones, which span in a larger area credibly resembling the variability in REE values.

Samples MW1, RW2 and TR2 seem to be outliers as compared with the rest of rocks. It is interesting to note that these limestone ashlars belong to diachronic structures, being correlated only by the high REE levels in the analyzed set. This feature could be related to peculiar sedimentary diagenetic conditions, post-depositional processes or even to restoration works.

3.5. Considerations on provenance of raw materials and construction phases

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 Lias (Pliensbachiense, 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

Table 3
Trace elements in Sagunto Castle samples determined through ICP-MS analysis.

Sample	Σ REEs	^{209}Bi	^{207}Pb	^{205}Tl	^{138}Ba	^{111}Cd	^{95}Mo	^{89}Y	^{88}Sr	^{64}Zn	^{63}Cu	^{60}Ni	^{59}Co	^{52}Cr	^{51}V	^{45}Sc	^{7}Li
RW1	14	< LOD	4	0.010	5	0.07	3	2	576	16	1.7	140	5	21	< LOD	1.3	0.6
RW2	84	0.07	26	0.04	6	0.09	2	9	2109	2	1.4	12	0.7	11	< LOD	4	1.9
RW3	1.2	< LOD	0.5	< LOD	16	0.006	0.5	0.2	143	26	1.2	420	33	2	11	4	0.6
RW4	9	0.001	5	< LOD	42	0.02	2	1.1	1907	5	0.9	62	2	7	25	1.3	0.8
RW5	3	< LOD	0.3	< LOD	5	0.005	0.3	0.6	364	28	0.2	466	20	3	< LOD	2	0.4
RW6	16	0.02	3	0.06	12	0.03	6	1.9	432	4	1.1	12	0.9	7	7	0.7	0.7
RW7	9	< LOD	3	< LOD	0.4	0.2	3	1.4	49	128	5	1584	93	25	5	6.8	2
RW8	14	< LOD	6	0.02	5	0.04	3	1.9	617	8	1.8	64	2	7	< LOD	1.3	0.9
TC1	29	0.05	46	0.06	2	0.14	2	2	718	45	3	18	1.1	8	4	1.7	3
TC2	28	0.05	44	0.05	6	0.14	2	2	694	43	3	18	1.04	7	3	1.7	3
TC3	1.9	< LOD	0.4	< LOD	5	0.005	0.08	0.3	196	43	1.2	572	37	1.5	< LOD	1.9	0.96
TC4	15	0.003	37	0.015	6	0.03	4	2	61	27	5	27	3	190	< LOD	1.6	1.1
TC5	11	0.012	22	0.03	22	0.10	3	2	62	18	5	9	1.2	7	< LOD	1.2	0.8
TC6	12	0.06	27	0.05	21	0.02	6	2	83	18	4	17	5	52	< LOD	1.3	1.7
TC7	13	0.02	30	0.03	0.8	0.12	12	2	160	36	4	51	1.7	18	20	1.8	1.9
TC8	4	0.007	4.5	0.012	9	0.03	9	0.9	110	39	4	86	4	39	78	1.5	3.8
TC9	8	< LOD	13	< LOD	27	0.05	3	1.5	46	30	1.9	191	7	10	< LOD	2	0.6
DT1	21	0.08	23	0.2	25	0.03	0.2	2	1255	< LOD	1.1	15	0.9	7	< LOD	1.1	1.5
DT2	12	0.02	16	0.04	45	0.05	0.9	1.3	62	9	1.9	24	1.6	24	17	0.7	1.1
RF1	12	0.02	26	0.08	16	0.24	0.8	2	78	19	3	19	1.5	88	22	0.6	0.3
RF2	12	0.03	8	0.03	13	0.03	0.5	2	53	9	2	21	1.6	16	12	1.1	0.7
RF3	7	0.04	65	0.06	18	0.02	0.6	1.1	57	14	2	21	1.1	9	20	1.0	0.5
FC1	18	0.06	6	0.2	7	0.006	0.2	1.7	528	< LOD	0.8	22	1.1	4	< LOD	0.8	0.5
FC2	20	0.03	10	0.04	17	< LOD	0.2	1.3	3003	1.0	2	28	1.5	11	5	1.2	1.6
FB1	25	0.15	14	0.4	8	0.06	0.3	2	577	2	2	20	1.2	10	< LOD	0.8	0.7
FT1	23	0.13	16	0.3	10	0.005	0.5	2	583	8	1.4	23	1.4	10	< LOD	0.7	0.6
FT2	20	0.08	36	0.3	7	0.05	0.99	3	85.7	15	4	22	3.1	31	59	2	1.4
TR2	115	0.09	5	0.07	26	0.09	2	22	287	88	30	46	19	63	82	8	0.03
TR3	14	0.007	0.9	0.007	14	0.02	0.13	3	246	4	< LOD	35	2	< LOD	7	1.1	0.003
IG1	19	0.010	20	0.02	9	0.05	1.1	2	1249	31	2	27	1.3	6	< LOD	1.1	1.6
IG2	12	0.02	28	0.03	23	0.12	11	1.5	150	33	4	48	1.6	16	19	1.7	1.8
IW1	9	0.014	10	0.04	14	0.05	1.1	2	67	33	5	13	1.9	107	49	0.9	2
MT1	18	0.002	26	0.05	16	0.05	0.06	2	1211	27	2	25	1.3	5	< LOD	0.8	0.5
HR1	10	0.04	15	0.09	9	< LOD	0.5	1.5	43.6	3	3	14	2	19	7	1.3	0.96
MW1	101	0.019	17	0.12	26	1.16	0.2	29	305	27	4	28	2	10	< LOD	1.8	0.55
NB1	18	0.03	20	0.04	13	0.07	0.5	2	89	35	4	27	2	103	14	1.7	0.94
CQ1	3	0.008	8	< LOD	47	0.10	14	0.8	76	44	5	389	15	29	135	6	2.47
CQ2	8	0.02	34	0.10	9	0.11	6	1.3	112	18.1	5	39	3	88	5	0.9	1.3
TQ1	6	0.011	12	< LOD	139	0.03	5	2	41	24.2	3	110	5	27	68	4	0.95
TQ2	5	0.003	1.8	< LOD	5	0.08	5.3	1.1	37	119	6	1228	77	55	182	16	2.63

Note: concentrations of elements expressed in μg/g.; the measurement error for each element in all the samples is lower than 1%. < LOD = under the limit of detection.

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 affinity with the Calvario Quarry materials (specifically, CQ2 sample). In the other studied structures, materials were possibly taken from Calvario and Theatre quarries, even if not thoroughly employed.

This first overview could suggest interesting historical and archaeological observations, especially by crossing the present results with the ones of the mortar analysis showed in Gallello et al. (2017) and Ramacciotti et al. (2018). First of all, limestone ashlars were used in most of the samples from buildings dating back to the Roman Ages, suggesting a prevalent use of raw materials from quarries outside the city, being exploited through Republican and Imperial periods. The occurrence of dolomitic-type stones similar to the rocks outcropping in the city quarries in almost all the investigated structures suggests the possible uninterrupted use of construction materials coming from the quarries of Calvario and Theatre. Though the exploitation of the two quarries inside the city during the Roman period would be possible, these cases of urban quarries could find a comparable example in the small quarry of PERI2 in Tarragona (Gutiérrez Garcia-M, 2011). Moreover, the use of these stones in the Republican Forum (FR), in the Republican Wall (RW) and in Diana Temple (DT), whose masonries were dated back to the Roman Republican period through mortar analysis (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

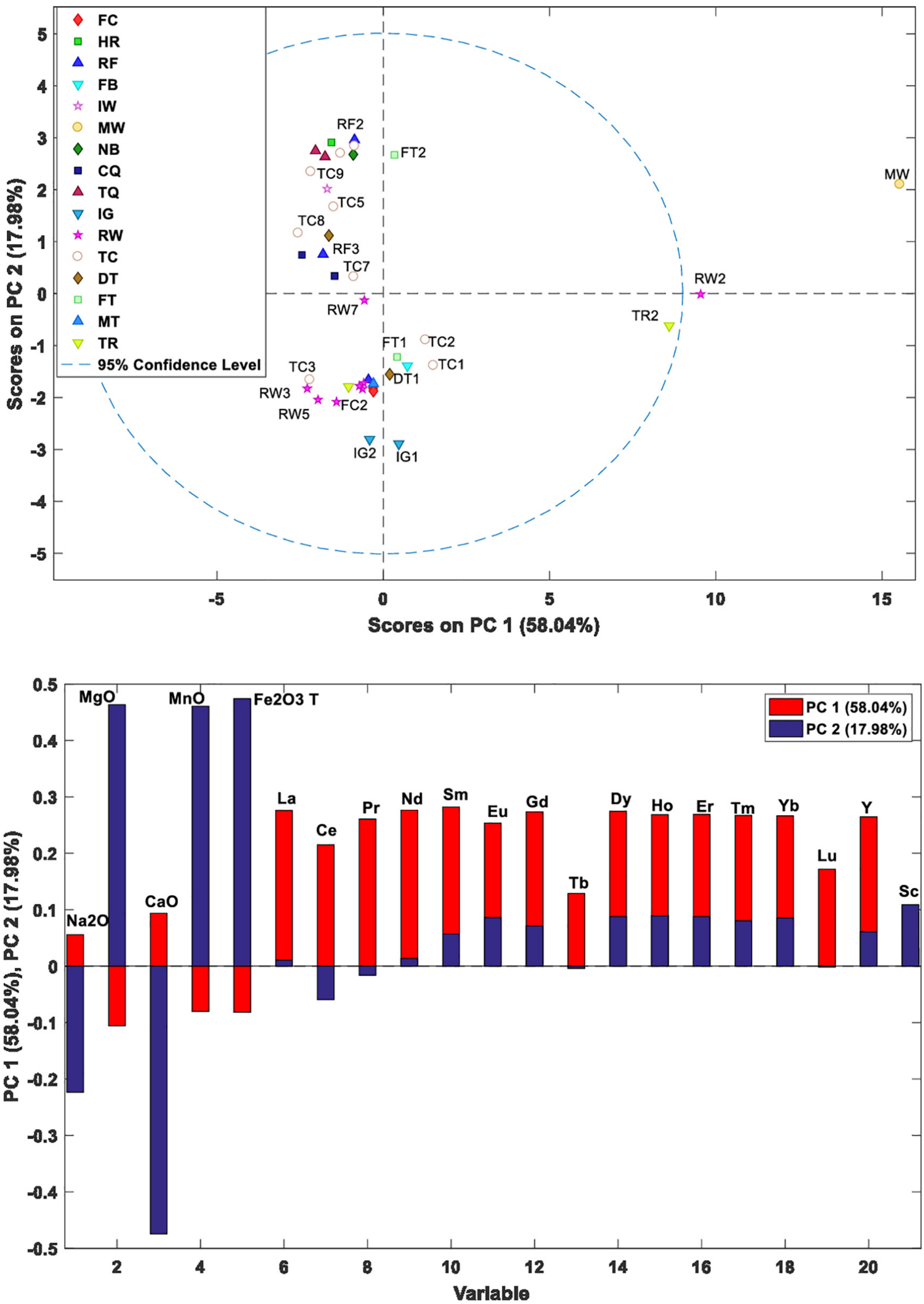

Fig. 3. Principal component analysis through selected oxides and REEs data. Scores biplot (top) and loadings plot (bottom).

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 considerate 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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