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Case study

Composition and technology of historical stuccoes coming from Grimani Palace in Venice (Italy)

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Abstract

Stucco samples moulded during a long period (from 1500 to 1700) were collected from Palazzo Grimani in Venice to study the binder and the working techniques. Three types of mixtures based on calcite and magnesite, on calcite, magnesite and gypsum and finally only on calcite were detected. The presence of magnesite in stuccoworks brings up questions about the employment of this substance, probably added to modify the workability and the aspect of the stuccoes.

Keywords: Stuccoworks; FT-IR; SEM; TG/DSC; Magnesite

1. Introduction and research aims

Since antiquity the stuccowork is known as sealing and filler building material between bricks and stones but with the passing of time its utility has been enlarged to the manufacturing of objects and to the surface covering until it became an important architectural decorative element and one of the most important expression style of artists in Italy. Although many important stuccoes exist in Italy and in Europe the analytical studies carried out on this type of artistic manufactures are very scanty. The knowledge of the stuccoes is a matter of interest from an historical point of view, since it is quite possible that the workers of various provenience and culture following each other in the course of the activity of a building decoration employed different mixtures or working techniques or composition of the stuccoes. Besides the knowledge of materials and methodologies of workmanship of stuccoes is a matter of primary importance on the choice of the most appropriate methods for their conservation [1]. This study has permitted to identify the materials employed on stuccoworks of Palazzo Grimani in Venice that have got a great artistic value either because they are dated or because they are attributable to a famous artist [2]. In fact some of stuccoes are attributed to Giovanni da Udine, an important artist who worked with Raffaello in Rome. Palazzo Grimani [3] is a 16th century building where in the first floor there are rooms decorated with splendid stuccoes and frescoes that can be attributed to workers of various origin and culture and to periods identifiable for a certainty. The work of the plastic model covers a period of three centuries, from 16th to 17th, which can be divided into four different time intervals [4]: 16th century wall finishings; a first cycle of stuccoes, of the year 1537/1540; a second cycle of stuccoworks, related to the years 1560–1570; a third cycle of 17th century stuccoes. The first stucco's cycle is located in Callisto and Apollo's rooms, and can be attributed for certainty to Giovanni da Udine, whereas all others are due to anonymous artists.

2. Experimental

The sampling has been preceded by an historical and artistic documentation and by visual observations of decorations in

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order to individualize the significant drawing positions for this study. All stuccoes taken into account belong to decorations and finishings of the walls. First of all the sample fragments have been englobed in conformity to ICR-CNR Raccomandazioni Normal 14/83 and have been analysed by optical microscopy (Olympus BX41and Olympus SZX9) and scanning electron microscopy (Jeol JSM 5600 LV) in order to study the petrographic texture, the stratigrapy and the morphology. The FT-IR spectroscopy (Nicolet Magna IR 750) and the EDX analysis have been used to obtain qualitative informations, respectively, on the species and the chemical elements found while the simultaneous thermogravimetry and differential scanning calorimetry (Netzsch STA 409/C) have been carried out to have quantitative data on the binding chemical compounds preceding a binding – aggregate separation.

3. Results and discussion

The optical and the scanning electron microscopy techniques show that the stuccoes representative of different age have some analogies in composition and in morphology. In particular some samples of the years 1560/1570 and the 18th century are fragments made of microcrystalline calcite and silicate aggregates made of metamorphic quartz and subordinately plagioclase, k-feldspar, pyroxene and traces of iron. The angular shapes aggregates have a very different granulometry distribution while the binding have got microcrystalline texture and homogeneous structure. Other samples related to the 1560/1570 period are made also by gypsum The samples made by Giovanni da Udine (1540) have been distinguished from the others stuccoes because have got sharp aggregates made up of only microcrystalline calcite (marble dust) while the binding is isotropic, microcrystalline and has got homogeneous structure; besides only these samples show a particular surface finishing with gold foil [5] on a red bolo.

The FT-IR spectroscopy confirms the identification of calcium carbonate, gypsum, magnesite, quartz, silicates and detects nitrates and weddellite that probably comes from traces of residuals of decayed organic material.

The registered thermograms of the bulk of all collected samples show a mass decrease in the range 630–800 °C, attributed to decomposition of calcium carbonate and generally in the range 380–500 °C ascribed to decomposition of magnesium carbonate [6]. Some of the thermograms also indicate a decrease of mass in the range 105–150 °C produced by elimination of the crystallization water of calcium sulphate [7]. In a few cases variations in the temperature ranges 220–270 °C and 360–420 °C have been observed revealing a further compound into the mixture of stuccoworks. They can be attributed to hydromagnesite (Fig. 1), considering the elimination of crystallization water in the first interval and the decomposition of the carbonate and hydrate in the second interval [8]. In only one case it has been registered a mass decrease in the range 365–440 °C in agreement to an exothermic peak; this phenomenon is attributed to the oxidation process of organic compounds.

The stuccoes of Giovanni da Udine have always a small but constant amount of magnesium carbonate, while in the other cases it is observed a significant variability also inside the same room; this could be a parameter that characterizes Giovanni da Udine samples. The magnesium carbonate could have been added in the mixing as additive to improve the aspect and the mechanical characteristics of the manufactures [9]. In fact from literature it comes out that if magnesite was present in raw materials as product for making the binder, hydromagnesite and not magnesite would have been produced

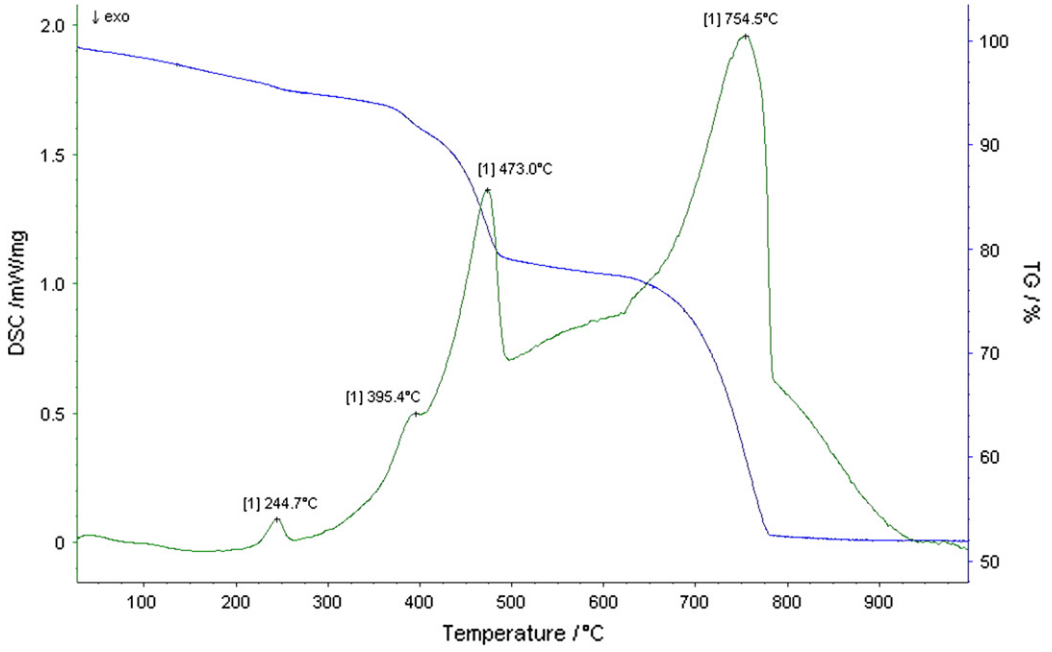

Fig. 1. Thermogram of sample PG6. The weight changes between 220 and 270 °C and between 360 and 420 °C can be attributed to the presence of hydromagnesite.

from magnesium oxide. For this reason we consider that magnesite was employed in the mixing with this crystal system to give peculiar physical, mechanical and aesthetic characteristics.

3.1. Chemical composition of the stuccoes

The analytical methods which have been applied provide qualitative and quantitative informations, allowing to describe the stuccoes in their chemical composition, as shown in Table 1. In some cases there is a deficiency of materials and the total percent composition is not 100%. This circumstance can be explained with the transfer of aggregating material in the binding during their separation, as a consequence of a strong grinding or for the presence of very thin aggregate.

In order to probe this hypothesis, the binding of three samples has been calcined to 1000 °C and the analysis by FT-IR indicate the presence of siliceous compounds.

4. Conclusion

The study allows the possibility to define the composition of the important stuccoes of Palazzo Grimani that represent a wide historical period of this artistic expression.

Depending on their composition, the mixtures for the stuccoes can be classified into three typologies, corresponding to three working techniques: the main typology is a mixture based on calcite and magnesite, the second one is a mixture based on calcite, magnesite and gypsum while the third one is a case based on calcite containing very little quantity of magnesite. This last typology is present in several rooms, with no correlation with other works; in fact, this technique has been used in Apollo's room by Giovanni da Udine, in the Chimney room and in the room of Doge Grimani, but it is also found, two centuries later, in the Main Hall.

The technique based on calcite and gypsum is found in two works of art in the Doge Grimani's room and in a gypsum calque in the Apollo's room and it can not be attributed to Giovanni da Udine because almost all the samples belong to stuccoworks dated after 1540 d.C. The mixture with calcite and magnesite seems to be widely applied. This mixture has been used by Giovanni da Udine in all his works which have been examined, using an amount of magnesite generally lower than 10% and in general lower than the determined quantity on the samples of the other authors. An interesting peculiarity is the systematic use of only calcite as aggregate. This technique distinguish Giovanni da Udine from all the other workers at Palazzo Grimani. Fig. 2 shows in a summary the ratios $CaCO_3/MgCO_3$ in the stuccoes; the rooms are ordered according to their age. It is evident that Giovanni da Udine was using a richer ratio in calcite (about 10:1) than the workers of the following ages. With regard to the other authors the use of different technologies is function of the ornament typologies. The comparison between similar works can be carried out for example analyzing the samples of the Chimney Room where the finishing of the two walls (samples PG3 and PG5) was done with the same execution technique. Samples PG1, PG2 and PG4, representing two finishing and an ornament of the same work, show a comparable composition. The comparison between various works located in the same

Table 1
Chemical compounds of the stuccoes

Room	Sample	Water (%)	Hydromagnesite (%)	Organic substances (%)	Gypsum (%)	$MgCO_3$ (%)	$CaCO_3$ (%)
Chimney	PG1, PG2, PG4	3.9				27–31	52–66
	PG3, PG5	1.5			<1	2	95
Grand Staircase	PG6	5.2	5		<1	26	47
	PG9				1.0	30	50
	PG7, PG10	5.2				30–32	52–58
Tribune	PG11	2.8			<1	24	71
Chapel	PG12	3.3			<1	29	54
	PG13	0.9				28	39
	PG14	2.5				14	76
Callisto	PG15, PG17	1.0			<1	8–13	82–90
	PG16	0.8			<1	–	96
Doge Grimani	PG18, PG29	2.4			30–33	3–9	43–52
	PG19, PG31, PG32, PG33, PG34	2.3			1–2	16–20	73–78
	PG30	2.7			<1	15	57
Courtney	PG20	1.8				11	81
Apollo	PG21, PG22, PG24, PG25, PG26, PG26, PG28	2.0			<1	6–8	86–88
	PG24					1	95
	PG27	2.4			33	13	42
Hall	PG35, PG37	2.8			<1	17–22	73–78
	PG36	1.0		1	2	2	91
	PG38	4.2			<1	27	49

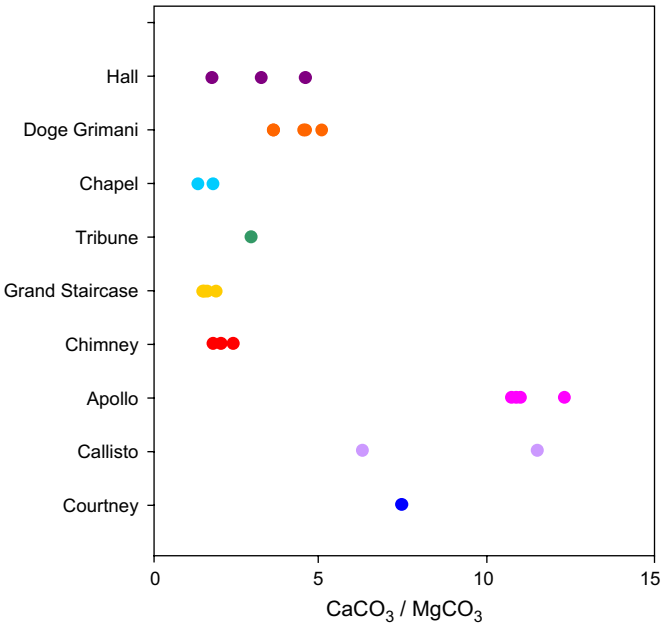

Fig. 2. Ratios $CaCO_3/MgCO_3$ in the various rooms.

room show that analogous techniques have been applied in the Grand Staircase, in the Chapel and in the rooms of Doge Grimani (apart from samples PG18 and PG29, of calcite and gypsum), whereas different techniques were applied in the Chimney Rooms and in the Main Hall, where just two works are comparable. The comparison between the different rooms indicate that the works of the Grand Staircase, of the Chapel and of the stuccoes of the Chimney Room (PG1, PG2 and PG4) can be related each other. The ornaments in the room of Doge Grimani are different from the previous ones and similar to that of the Main Hall, even if the last ones are dated to the 18th century.

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