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Chemical and isotopic investigations on the deterioration of the Monumental Complex of S. Pietro in Corte in Salerno (Italy) caused by the rising waters.

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***Abstract* - Two important streams are visible in the upper part of the city of Salerno (Italy), which are buried under the city, feeding the underground aquifer of the historic center. Until the beginning of the last century, this water was collected with wells present in churches and convents and fed mills, fountains, wash houses, thermae, and balnea. The most important testimony of the Roman period is the frigidarium discovered seven meters below the palatine chapel of Prince Arechi in 1970. In the underground area, frescoes from an early Christian church have also been brought to light. In the upper part of the underground area up to above street level, the formation of saltpetre efflorescence is observed.**

In this work, the plausible origin of these efflorescences was investigated through the isotopic determination of nitrogen. Moreover, through the chemical analysis of waters, which of the two main streams (the Rafastia and the Fusandola) fed the ancient frigidarium was identified.

Keywords: cultural heritage, water quality, saltpetre efflorescences, nitrogen stable isotope ratio

I. INTRODUCTION

The Roman colony of Salernum was founded in 197 BC on the southern coast of the Tyrrhenian Sea. One of the reasons for choosing the place is probably the abundance of water that comes from the Bonadies hill of about 300 m above sea level. During the Roman period, the perimeter of the city of Salerno was confined by two small rivers named: the Rafastia (Nord-West) and the Fusandola (Nord-Est). Inside this area were the defensive walls. Now there are few traces of the Roman city because many buildings were built during the Middle Ages, often on areas buried by the debris of the floods of these rivers which periodically invaded the city [1, 2, 3].

In the 8th century AD, the Lombard prince Arechi II erected in Salerno, the capital of his kingdom, an autonomous structure intended for the function of the palatine chapel that now is the S. Pietro in Corte Church. In the Middle Ages, these environments were designated as the ideal place for graduation ceremonies of the Salerno Medical School, the oldest Medical School of Europe, while during the First World War, they became a military storage area [4].

Starting from the 1950s, the presence of a puddle in the underside of the church has been documented by some bakers who carried out their activities under the church and used to take water from this well.

In 1970, the collapse of the floor at street level showed some frescoes on the underside of the Monumental Complex of S. Pietro in Corte (see Figure 1 for section and planimetry). Subsequently, in 1980, an earthquake occurred in Salerno and surrounding cities causing the fall of the total floor of this monumental complex.

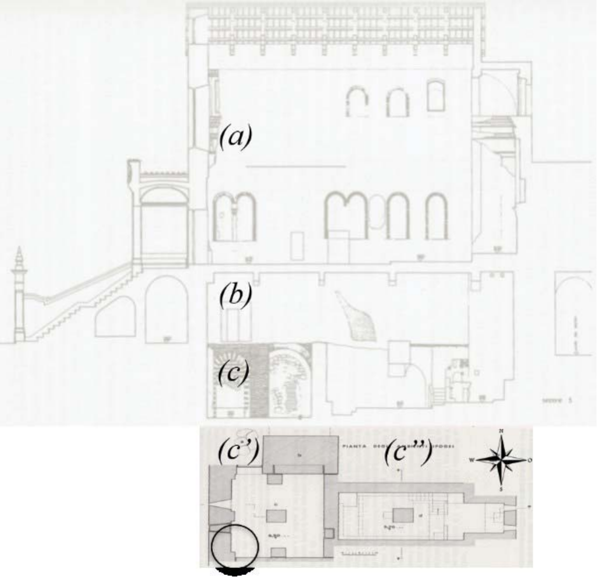

Fig. 1. Section of Monumental Structure and planimetry of the hypogean section: (a) Palatine chapel; (b) floor at street level; (c) hypogeum; (c') frigidarium map with a circle to indicate the puddle; (c") paleochristian church map.

These episodes prompted archaeologists to carry out some excavations that have brought to light two environments at about seven meters below the current street level: one in the East Side (Figure 1c") containing a temple of Priapus, later become a Paleochristian Church having some wall frescos, and another in the West Side (Figure 1c') consisting of the thermal structure of a frigidarium pool dating back to the 1st or 2nd century AD [4]. Part of the spa complex was identified with the excavations in the Palazzo Fruscione that is located on the north side, in front of S. Pietro in Corte, separated by a path of few meters wide, now known as Vicolo Adelberga. Most probably, the discovered puddle that fed the frigidarium (Figure 2) was the same used by local bakers for taking water.

Fig. 2. Puddle close to frigidarium.

Avoiding the deterioration of several frescoes found in the hypogeum of the Monumental Complex of S. Pietro in Corte is of great interest. The degradation of cultural heritage exposed to atmospheric and water pollution has become an increasing concern over the past decades, highlighting the need to know the origin and the evolution of contaminants to preserve it [5, 6].

One of the most important phenomena that the superintendence of cultural heritage has to deal with is the formation of efflorescences that disfigure the frescoes and reform a few months after their mechanical removal [7]. The reaction responsible for the formation of saltpetre efflorescences can involve nitrates present in the infiltration groundwater or atmospheric nitrogen oxides (NO_x). Different air pollutants (NO_2, SO_2, and CO_2) have negative effects on cultural heritage due to their chemical reaction with raw materials, so several investigations were conducted to find simple methods necessary to monitor their concentration [8, 9, 10, 11].

An important parameter that helps to assess the origin of a sample is the stable isotope ratio [12]. The preferred method for analysis of the stable isotope ratio at natural abundance is Isotope Ratio Mass Spectrometry (IRMS) because of its relatively high accuracy (0.1‰) and sensitivity (up to 0.01‰) [13]. This mass spectrometric method gives the stable isotopic composition of a sample relative to that of reference material. To avoid sample pre-treatment, an elemental analyser can be coupled to the IRMS system [14]. The IRMS technique demonstrated the potential to differentiate between samples from different sources [15], e. g. in the investigation of complex forensic cases by identifying different sources of the same type of explosive, namely ammonium nitrate. In some cases, a combination of the nitrogen, oxygen, and hydrogen isotope values is needed to obtain complete discrimination of sources [16]. Carbon stable isotope ratio, for example, was recently employed in the analysis of food [17], commercial cleaning products [18], atmospheric pollution [19], and so on [20, 21]. Nitrogen stable isotope ratio expressed as $\delta^{15}N$, indeed, allows discriminating the sources of a specific nitrogen compound such as in sediments where it indicates the contribution of human waste to total nitrogen [22]. $\delta^{15}N$ has been used as an important tool in differentiating sources of nitrate (NO_3^-) contamination and investigating the nitrogen cycle in ecosystems [23, 24].

In this work, we tried to answer two important questions raised by archaeologists: which of the two streams (the Rafastia or the Fusandola river) feeds the aquifer that fed the ancient frigidarium and the nature of the saltpetre efflorescences that occur in the upper part of the excavation and constitute a great risk of degradation of all the underground environments.

II. MATERIALS AND METHODS

Sodium nitrate ($NaNO_3$), sodium sulfate (Na_2SO_4), sodium carbonate (Na_2CO_3), and sodium hydrogen carbonate ($NaHCO_3$) were purchased from Sigma-Aldrich (St. Louis, MO, USA).

Water sampling of the puddle near to the frigidarium of the Monumental Complex of S. Pietro in Corte and the Rafastia and the Fusandola rivers was performed for about six months. Glass bottles (volume of ~ 250 mL) were filled with water and immediately closed and stored between 4 and 7°C before the analysis. During the same time, the efflorescences were also sampled.

Anion-exchange chromatography analyses were performed using a Thermo Scientific-Dionex™ Aquion™ ion chromatograph equipped with a Dionex IonPac AS23 carbonate eluent anion-exchange column. Nitrate (NO_3^-) and sulfate (SO_4^{2-}) ion concentrations (expressed as mg/L) were obtained using calibration curves prepared employing $NaNO_3$ and Na_2SO_4 as standard.

A Delta Plus V isotope ratio mass spectrometer (ThermoFinnigan, Bremen, Germany) equipped with a Flash EA 1112 Elemental Analyzer (ThermoFinnigan) was used to measure $\delta^{15}N$. The nitrogen isotope ratio was expressed in δ‰ relative to atmospheric N_2 (R=0.003676) according to the following equation:

$$\delta\,^{15}N = (RSA-RREF)/RREF \qquad (1)$$

-RSA is the respective isotope ratio of a sample (number of ^{15}N atoms/number of ^{14}N atoms or as approximation $^{15}N/^{14}N$);
-RREF is the isotope ratio of the relevant internationally recognized reference material (AIR).
The delta values are multiplied by 1000 and are expressed in units "per mil" (‰). $\delta^{15}N$ was calculated against L-glutamic acid USGS 40 and potassium nitrate IAEA-NO_3, purchased from the International Atomic Energy Agency (IAEA). The precision of measurement, expressed as one standard deviation, was 0.1‰.

III. RESULTS AND DISCUSSION

In the first part of this work, we investigated which one of the two important streams (the Rafastia or the Fusandola) that are buried under the city of Salerno, feeding the underground aquifer of the historic center, reach the puddle discovered in the frigidarium of the Monumental Complex of S. Pietro in Corte.

To answer this question, we sampled the waters of the two streams and the well in the hypogeum for about six months and analysed them by ionic chromatography. The most significant of all the determinations are reported as the average nitrate concentration in Table 1.

Table 1. Average nitrate concentration detected at the three different sampling points with their altitude and geographic coordinates.

	Altitude over the sea (m)	Geographic position	Nitrate average concentration (mg/L)
S. Pietro in Corte	19±1	40.658 N 14.755 E	69±0.1
Rafastia	87±1	40.687 N 14.687 E	67±0.1
Fusandola	81±1	40.680 N 14.753 E	26±0.1

Taking into account these results, we moved to the characterization of the source of salpetre efflorescences that occurs on the wall of hypogeum near to several frescoes, damaging them as shown in Figure 3.

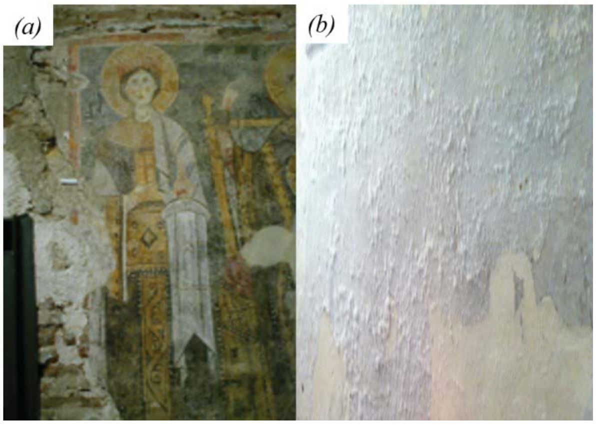

Fig. 3. (a) damaged fresco and (b) salpetre particular.

First of all, ionic analysis of efflorescences proved the predominance of salpetre (minimum 90 % w/w of nitrate) with a small fraction of sulfate (less than 10 % w/w).

In our case, a possible source of saltpetre is represented by the aquifer that fed the ancient frigidarium and flows in the puddle. The high concentration of nitrates found in the puddle could cause efflorescence.

In order to resolve this issue, we performed a $\delta^{15}N$ isotopic analysis on the nitrates recovered from the waters of the puddle and salpetre by using isotope ratio mass spectrometry (IRMS).

The results of these analyses are reported in Table 2.

It is quite evident that the nitrates present in the water have a different origin from those of the efflorescence present on the walls. Therefore, the cause of the deterioration of the walls should be sought elsewhere.

Table 2. Nitrogen stable isotope ratio value (expressed as $\delta^{15}N$) of the nitrate samples.

	$\delta^{15}N$ (‰)
Nitrate from the water of puddle	+2.9±0.1
Nitrate from saltpetre	+9.3±0.1

The value of $\delta^{15}N$ +2.9‰ is generally consistent with the inorganic nitrogen compounds and this result is explained considering that the nitrates determined in the puddle certainly originate from the leaching of the fertilizers used in the agricultural lands crossed by the streams [25].

Generally, the expected nitrogen $\delta^{15}N$ range of inorganic fertilizers is between -2 and + 4‰ [26]. The high $\delta^{15}N$ value of nitrate of the efflorescences is related to degradation phenomena of organic substances whose origin is external to the perimeter of the monumental complex. Moreover, we also discovered the formation of the same salts, with a similar isotopic delta value (8.6‰), inside the ancient Palazzo Fruscione which is located on the north side of S. Pietro in Corte. From historical pieces of information [27] and Geological surveys of the historic center of Salerno, it has been highlighted the presence of a significant sedimentary layer that makes the upper layer waterproof to the aquifer, thus preventing the mixing of groundwater with surface water. We found that the road that divides the two buildings was formerly crossed by drains of rainwater and in the twentieth century by the pipes for collecting wastewater that probably does not support the anthropogenic load of the neighbourhood [28, 29, 30]. Therefore the impermeable layer of the subsoil protects the hypogeum walls only for the first few meters, preventing the spring and clean waters of the puddle from exceeding it, but unfortunately, the surface dirty waters, which favour the formation of saltpetre efflorescences, permeate through the walls containing the frescoes and the upper layers of the monumental complex.

IV. CONCLUSIONS

In this work, we have identified that the Rafastia river fed the ancient frigidarium of the Monumental Complex of S. Pietro in Corte, in Salerno (Italy). Furthermore, the nature and the source of the saltpetre efflorescences, that occur in the upper part of the excavation, was investigated.

In particular, we used nitrogen stable isotope ratio to discover if the salts contained in the puddle of frigidarium are the cause of the occurring efflorescences, which represent a great risk of degradation of all the underground environments. $\delta\ ^{15}N$ measurements have shown that the nitrates present in the groundwater have a different nature than those of saline efflorescence. Therefore, the cause of the deterioration of the walls could be the surface dirty waters that permeate through the walls containing the frescoes and the upper layers of the monumental complex.

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