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Provenance Study of Gypsum Black Crusts

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Abstract: $CaSO_4^-$ black crusts are the major cause of the deterioration of cultural heritage monuments. Gypsum black crusts are formed on marble or other carbonate rocks as a result of the reaction of atmospheric sulfur with the calcium of the stone causing erosion of its surface. Samples of $CaSO_4^-$ crusts were collected by scraping off about 1 g of the layer of decayed carbonate rocks. A total of 18 samples from the archaeological site of Vryokastro at Kythnos island in Greece, were collected. These salts may have originated from different natural and anthropogenic sources. Understanding this deterioration process is crucial for the restoration/conservation of cultural heritage monuments. The natural sources include biological sources, construction materials, rainwater, marine spray, and pyrite oxidation within the rock substrate. Anthropogenic sources include pollution from fossil fuels. The oxygen and sulfur isotopes can help to discriminate the S-origin of black crusts. The isotopic analysis was conducted in the Stable Isotope Unit of the Institute of Nanoscience and Nanotechnology (NCSR Demokritos). For S isotope analyses, sulfate minerals were dissolved in deionized water and subsequently precipitated as $BaSO_4$. Sulfur isotopic compositions were measured after the conversion

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of $BaSO_4$ to SO_2 using an elemental analyzer (Flash EA device) coupled with an isotope ratio mass spectrometer.

Keywords: Sulfur isotopes, Oxygen isotopes, Gypsum crust, Monument degradation

Introduction

Environmental degradation of historic mortars is a main threat to the safe preservation of historic monuments (Yates, 2003; Sabbioni, 2001; Zappia, 1994). Climatic and environmental conditions are often very severe for construction materials, namely in the presence of high humidity or in direct contact with water. Agents of decay such as sulfate attack, acid attack, leaching action, salts attack, damage due to frost and fire, poor mixing and choice of constituents and many more can cause extensive cracks and total disintegration of historic constructions (Sabbioni 1998;Grosssi & Brimblecombe, 2007). The sources of mortar decay could be physical-related to physical variations of water inside masonry (evaporation, capillary flow, ice formation, etc.) or chemical (formation of expansive products such as ettringite and thaumasite).

Sulfate salts crystallizing on the surface of building stones are one of the most important factors of monument degradation. The natural sources of these salts include biological sources (Hanoso, 2006), construction materials (Vallet 2006; Schleicher 2010; Kloppmann et al., 2011), rainwater, marine spray (Kloppmann et al., 2011), and pyrite oxidation within the rock substrate (Kramar, 2011). Anthropogenic sources include pollution from fossil fuels (Kramar, 2011). The microstructure, the mineralogical and chemical composition of historic mortars have been examined to some extent using traditional techniques of instrumental analysis and microscopy, but the literature is dispersed and there is no generally accepted or preferred protocol for their investigation [Dotsika et al., 2009). Recently it has been shown that the stable isotopes of carbon and oxygen offer considerable potential in the investigation of lime mortar and plaster but relatively little work has been conducted so far (Dotsika et al., 2018).

The oxygen and sulfur isotopes can help to discriminate the S-origin of black crusts (Vallet, 2006; Schleicher, 2010; Kloppmann et al., 2011;Kramar, 2011; Schwigstillova, 2009). Black crusts have $\delta^{34}S$ and $\delta^{18}O$ values around 0 ‰ vs. CDT and +11 ‰ vs. SMOW respectively, which is typical for atmospheric sulfates (air pollution). Marine sulfate ranges around 20-21 ‰ *vs.* CDT and around +9,5 ‰ *vs.* SMOW for $\delta^{34}S$ and $\delta^{18}O$ respectively. The data from Kythnos Island (Greece) show clear isotopic contrasts between black crusts, which can be considered as representative of a predominantly atmospheric origin [urban air present value between 0‰ and +20‰ (Newman et al., 1991), and marine sulfate (marine aerosol present value around 20‰), (Siedel & Klemm, 2000). These potential end-members of sulfate contamination have distinct and well-defined isotopic signatures.

Archaeological Informations

An island with a long history and particular archaeological importance is Kythnos, which is situated between Kea and Serifos. The ancient city of "Vryokastro", on the island's northwest shore, was a fortified polis that was continually inhabited from the first millennium B.C. to the sixth or seventh century A.D (Figure 1). The remains of the ancient city occupy an area of approximately 28,5 hectars, including the small islet of Vryokastraki, which was connected to the shore in antiquity by a narrow isthmus. During the systematic investigations that have been in progress since 1990 (survey and subsequent excavations) numerous finds and several ancient structures, such as temples, public buildings, houses, port facilities, burial monuments, etc., have been brought to light. These discoveries have provided valuable insights into the urban planning of the city and the sociopolitical and economic development of the ancient community.

Regarding the construction of the buildings, the island's ground is composed of various types of crystalline slates (metamorphic rock) with intervening marble horizons. Slate and limestone appear to have been used extensively for the buildings of the ancient city, and the discovery of marble fragments of architectural elements from the sanctuaries of the Upper Town confirms its parallel use. Several samples of marble were chosen in order to identify the marble's provenance. A selection of numerous stones, coquina rocks, slates, and mortars that were structural components of the buildings and belonged to structures of various chronological periods was made during the field inspection of the intramural sanctuaries located on the Middle Plateau.

Figure 1. Aerial photograph of Vryokastro

Figure 2 . Sanctuary dedicated to Artemis and Apollo

More specifically, the chosen specimens were procured from the Upper Town precinct, housing the Late Classical sanctuary of **Asklepios,** Aphrodite, and the Samothracian Gods (Mazarakis - Ainian, 2017, 2019), as well as from the Archaic sanctuary dedicated to **Artemis and Apollo** (Mazarakis - Ainian 2017, 2019) (Figure 2.). Furthermore, samples were taken from a public building of the Hellenistic period identified as the Hellenistic Prytaneion of the Kythnians and from the Sanctuary of Demeter and Core on the Acropolis Hill (Mazarakis – Ainian, 2019).

Sampling

To gather crust samples, approximately 1 gram of decayed carbonate rocks was scraped off. A total of 18 samples were collected from the Vryokastro archaeological site on Kythnos island in Greece. Comparative samples were also taken from four historic constructions - Hellenistic, Late Roman, Byzantine, and Ottoman - located in Anaktoroupoli, Marmarion tower in Kavala, Fortification walls in Drama (n=4), and Funerary monuments in Makrygialos (n=4) in North Greece. Additionally, a sample was collected from an area in Athens that is heavily affected by atmospheric pollution.

Methods

The isotopic analysis was conducted in the Stable Isotope Unit of Institute of Nanoscience and Nanotechnology (NCSR Demokritos). For S isotope analyses, sulfate minerals were dissolved in deionized water and subsequently precipitated as $BaSO_4$. Sulfur isotopic compositions were measured after conversion of $BaSO_4$ to SO_2 using an elemental analyzer (Flash EA device) coupled with an isotope ratio mass spectrometer. Sulfur isotope measurements were performed with an analytical error of better than ±0.3‰ and results reported in delta notation ($\delta^{34}S$) as ‰ deviation relative to the Cañon Diablo Troilite (CDT) standard. Oxygen isotope measurement results were performed with an analytical error of better than ±0.3‰ and are expressed in delta notation ($\delta^{18}O$) as ‰ deviation relative to Vienna Standard Mean Ocean Water (V-SMOW), according to:

$\delta = [(Rsample - Rstandard) / Rstandard] \times 1000$ (1)

where R is the ratio between the heavy and the light isotope, in this case $^{18}O/^{16}O$ or $^{34}S/^{32}S$. The reported values are the mean of two or more consistent measurements of each sample.

Results and Discussion

In table 1 and Fig.4 we present the isotopic values of oxygen ($\delta^{18}O$) and sulfur ($\delta^{34}S$) of black crusts from the five sampled areas. The shaded areas are the mean isotopic values of black crust samples from different sampled monument of France (Kloppmann et al., 2011) and Italy (Longinelli & Bartelloni, 1978) as gathered from the literature. Chemically, all analyzed black crusts are dominated by Ca and SO4, (up to 85 wt). Both sulfur and oxygen isotope ratios of all analyzed black crusts (Fig. 4) from Kythnos show $\delta^{34}S$ values from −2 to +8‰ and $\delta^{18}O$ from +6 to + 12‰, and these values stay within the ranges of black crusts observed in literature (Table 1, Fig.4).

Table 1. $\delta^{34}S$ and $\delta^{18}O$ for black crusts

Material	Location	Sites	$\delta^{34}S$	$\delta^{18}O$
black crusts	Greece	Anaktoroupoli, Kavala	4.7	3.5
black crusts	Greece	Marmarion tower, Kavala	7.5	5.4
black crusts	Greece	Fortification walls, Drama	2.1	3.2
black crusts	Greece	Funerary monuments, Makrygialos	2.2	4.7
black crusts	Greece	Athens	-1.2	11.9
black crusts	France	Bourges, Chenonceau, Versailles, Marseille, Chartes	-1.4 to 7.4	6.3 to 12.4
black crusts	Italy	San Marco, Venice	4 to 6	7 to 9
black crusts	Greece	Kythnos 1	-2 to 2	8 to 12
black crusts	Greece	Kythnos 2	7 to 8	6 to 12

There are, though, significant differences between the two study sites. Whereas all $\delta^{18}O$ values for Kythnos 1 and 2 are close to 9-10‰ $\pm$ 2‰, $\delta^{34}S$ values are different, Kythnos 1 being situated around 0 $\pm$ 2‰, while Kythnos 2 are closer to + 7-8‰. The oxygen in sulphates comes from various sources such as air (with a delta value of +23‰ for gaseous O2), water (with delta values ranging from -11 to -5‰ (Dotsika et al., 2010; Dotsika et al., 2018b), and diesel combustion residues (with a delta value of 24.5‰ according to (Rivas et al., 2014). The contribution of each source depends on the reaction mechanism used, whether it is hydrolysis-oxidation or oxidation-hydrolysis, as noted by Holt et al. studies in (Holt et al., 1981a,1981b). So, the differences in the $\delta^{18}O$ of the black crusts could be derived as a result from two Oxygen sources: low $\delta^{18}O$ values of rain water (variable negative values) and high $\delta^{18}O$ values of sulfates contained in dusts. Therefore, the differences in the value of $\delta^{18}O$ in black crusts may reflect slight climatic differences, a different signature of rainfall, and/or variable participation of 'polluted' sulfates. In our case, the continental effect (isotopic gradient of Greece is around –0.2‰/100 km (Dotsika et al., 2010) should not affect the O isotope signal given the very small spatial rain distribution of Kythnos Island. These values, Kythnos 1, are very similar to Bourges and Versailles (Kloppman et al., 2011), that are attributed to the isotopic difference of local meteoric conditions. This is not our case due to the small dimension of the Island and also the samples coming from the same area. The $\delta^{34}S$ values of Kythnos 1 vary within a very limited range around 0 $\pm$ 2‰ ‰ *vs.* CDT. These values are typical of atmospheric sulfates ($\delta^{34}S$ and $\delta^{18}O$ values range around 0 ‰ *vs.* CDT and around +11 ‰ *vs.* SMOW respectively). Newman et al. (Newman et al., 1991), suggests that this participation surpasses the other sources.

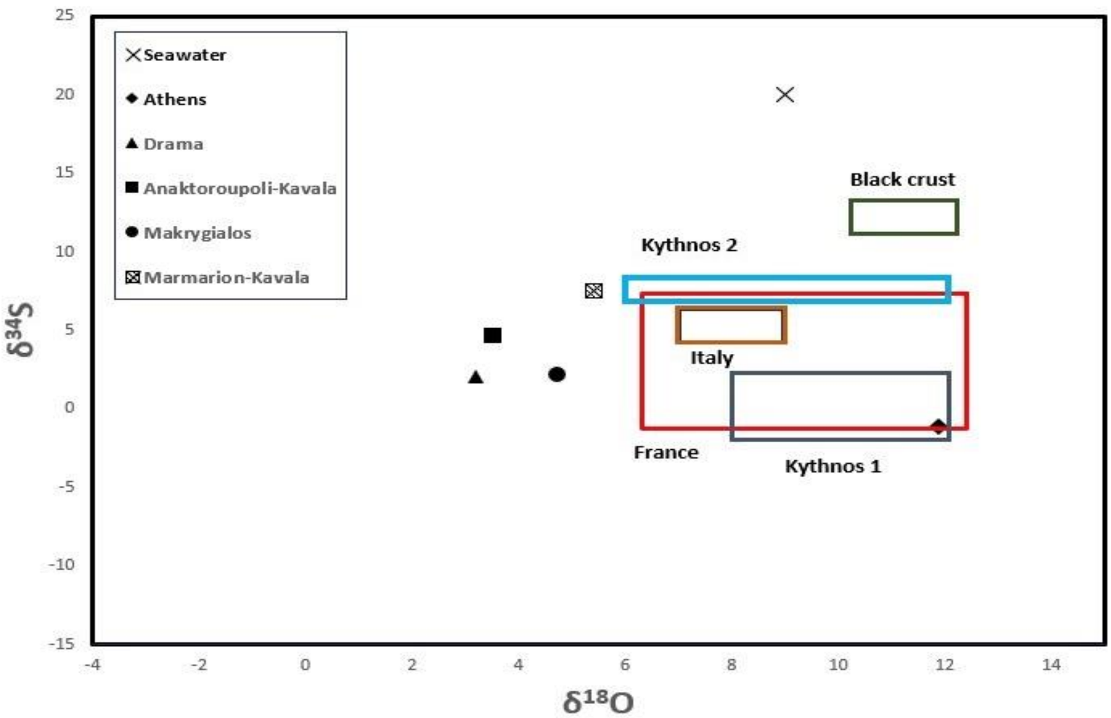

Figure 3. $\delta^{18}O$ vs $\delta^{34}S$ for black crusts

The black crusts of Kythnos 2 are significantly enriched in $\delta\,^{34}S$ by 7‰ with respect to Kythnos 1 isotopic values. This enrichment in heavy sulfur probably reflects a sea spray contribution (Siedel & Klemm, 2000). Similar values show also the black crust from San Marco Cathedral, Venice (Longinelli & Bartelloni, 1978). Probably the difference between the two sites is attributed to the orientation of the buildings, which receive winds from different directions, charged with more or less sea droplets. The competitive role of the sulfates of different origins was revealed (marine versus pollution).

Conclusions

In this preliminary study it is evident that the stable isotope analysis of the ^{34}S and ^{18}O can successfully discriminate the origin of the black crust on the deteriorated surface of the Kythnos monuments. The competitive role of the sulfates of different origin was revealed (marine versus pollution). In general, the isotopic values appear to be a useful tool to diagnose mortar degradation and determine the different sources of decay.

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

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