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STABLE ISOTOPE ANALYSIS (^{13}C AND ^{18}O) AS A TOOL TO INVESTIGATE PARTICULATE MATTER IN HISTORIC LIBRARIES

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SCIENTIFIC PAPER

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Micro-samples of loose dust were obtained from a collection that is preserved on open display at the Hellenic Literary and Historical Archive, a historic library with significant levels of particle pollution. The samples were analysed using scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDXA). Qualitative point EDXA was used to identify the characters and origins of individual particles, while bulk analysis was achieved by rastering the electron beam over whole samples. Stable isotope analysis ($\delta^{13}C$ and $\delta^{18}O$) was conducted in order to evaluate the origin of dust and to determine potential dust recrystallization processes.

1 Introduction

The deposition of dust particulates (>0.1 μm) in museum and historic interiors soils objects on open display, reducing their aesthetic value.[1-3] Additionally, dust deposition poses a threat to the physical integrity of books.[4-5] Recent research suggests that in humid conditions dust becomes cemented on the surface of the book turning the cleaning process into an additional source of damage.[6] Dust removal in historic interiors is a major investment since it encompasses the most expensive preventive conservation task.[7] The reaction of visitors towards dust settlement in historic interiors was examined[8], demonstrating that they appear concerned about the potential risks for the objects.

The deposition of dust has caused extensive soiling on books at the Hellenic Literary and Historical Archive which is why the characterisation of the source of soiling is attempted. Previous investigations on dust analysis developed the application of various methodologies in order to investigate the issue of dust generated soiling.[9-12] Despite the fact that dust research developed a number of functional techniques to monitor dust in the atmosphere and the rate of dust deposition,[13-14] the identification of the source of dust was recently examined.[14] Dust atlas and dust identification toolkit was developed by Lloyd et al.,[14] which is a useful and functional guide to low-tech dust analysis. This is a highly effective tool that can be easily adopted by preventive conservators in order to identify the potential sources of dust and instigate appropriate mitigation strategies.

This paper aims to present the application of high precision analysis, expressed in units of parts per thousand on dust identification. A combination of analytical techniques is applied to determine the origins and the characters of dust particles. SEM/EDX was applied to determine the elements and the morphology of dust particles, while stable isotope analysis was performed to detect the isotopic fingertip of dust particles and hence determine their origin. Stable isotope analysis, was performed to aid the characterisation of different particles and make possible to characterise the atmospheric particles such as combustion products. Oxygen and carbon stable isotopes (^{13}C and ^{18}O) demonstrate a good potential in providing proxies, for the conditions of formation and the origin of the carbonates.[15-16] Isotopes demonstrate a ratio that is expressed by δ value: Stable isotope compositions of low-mass (light) elements such as oxygen, hydrogen, car-

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bon, nitrogen, and sulfur are normally reported as δ values, δ values are reported in units of parts per thousand (denoted as ‰), relative to a standard of known composition. Therefore, this paper aims to present a novel application of stable isotope geochemistry in the determination of the origin of dust. The isotopic signature of dust particles (coarse fraction >2 μm) will hopefully make possible to safely determine the source of dust and inevitably enable the design of suitable dust mitigation strategies.

2 Materials and Methods

2.1 Sampling

The Hellenic Literary and Historic Archive (E.L.I.A.), is housed in a historic building situated in the centre of Athens. E.L.I.A. is located in a privately owned five-storey neo-classical building, constructed around 1930, near the Cathedral of Athens at Philotheis Str. in Plaka. It is located in a historic building made of limestone and the walls are covered with plaster. The construction materials are briefly presented here because they are likely to affect the type of indoor and outdoor particles inside the Archive. The building houses: the department of the Historical and Literary Archives, the Library, the reading room, the collections of the Press and the administration offices. The samples were obtained from the department of the Historical and Literary Archives. The books are preserved on open display and visitors are allowed to access them for study. This building structure provides a very short thermal lag; it is poorly insulated against environmental changes, which means that the changes in the external environment affect directly the indoor environment of the historic library. The internal environment is uncontrolled. The building has one main entrance and one fire exit. A sample size representing approximately 10% of the library books was chosen for analysis. This sample size was considered representative of the average dust deposition on each book. All the books were 19th century edited volumes of scientific journals as well as novels published in Greece and preserved in the Hellenic Literary and Historical Archive. The dusts were brushed from the head of the books and then collected in a form of powder in an overall sample.

2.2 Analytical techniques

The dust samples were mounted on adhesive carbon disks and then located on stubs suitable for SEM analysis.[17] The samples were carbon coated before analysis, to minimise effects due to charging. Major and minor elements for dust samples were analysed using a FEI/Quanta Inspect D8334 scanning electron microscope, fitted with an energy dispersive X-ray analyser at NCSR Demokritos in Athens, Greece. The working distance was 10 mm and the accelerating potential 20 kV. X-ray accumulation times were typically 100 s. The detector was calibrated with a range of pure elements, synthetic oxides and well characterized minerals. Accuracy and precision for major components, determined upon well characterised silicates, are typically better than 5% relative, although for these very inhomogeneous samples, errors may be greater than this and are difficult to determine. Oxygen was not analysed directly but calculated on the basis of stoichiometry.

For bulk analysis, the SEM beam was rastered across each sample, at the lowest practicable magnification to give the maximum analysed area. Accuracy and precision in bulk analysis of dust samples were expected to be somewhat reduced because dust is composed of particles and fibres and the areas analysed, typically only 1-3 mm across, may not have been fully representative. For comparative purposes the results were normalised to 100%. These values represent an approximation of the composition of the inorganic components of the materials analysed, and should give a good reflection of the relative variations of the inorganic compounds present. Note that they do not include organic components or water. To identify the compounds or minerals present, point X-ray analyses were also undertaken on 20-30 particles observed in a back-scattered image of each sample, and the compounds identified on the basis of the qualitative X-ray spectra. Imaging was performed using a backscattered electron (BEI) and a secondary electron detector (SEI). In the backscattered images compounds rich in heavy elements such as iron and lead appear brighter than those rich in light elements such as carbon or oxygen. As a result, backscattered electron images demonstrate the make-up of the dust particles, since sharp changes in grey levels represent different compositions. On the other hand, secondary electron images demonstrate the morphology of the dust particles and fibres, giving an enhanced three dimensional view of the particles.

The isotopic analysis was performed in the Stable Isotope Unit of the Institute of Material Science (NCSR Demokritos, Athens, Greece) on a Thermo Delta V Plus IRMS equipped with GasBench II device and a Flash EA 1112 Thermoscientific device. The samples of dust were grounded to a fine ground powder and then diluted in ortho-phosphoric acid. The CO_2 produced was measured in the Isotope Ration Mass Spectrometer. The isotopic ratios of $^{13}C/^{12}C$ and $^{18}O/^{16}O$ were determined in units of parts per thousand (denoted as ‰ or permil), relative to a standard of known composition. δ values are calculated by equation (1) :

$$\delta(\text{in } ‰) = (R_x / R_s - 1) \cdot 1000 \quad (1)$$

where R denotes the ratio of the heavy to light isotope (e.g., $^{18}O/^{16}O$), and R_x and R_s are the ratios in the sample and standard, respectively. The $\delta^{13}C$ and $\delta^{18}O$ was measured with an accuracy of 0.1‰ estimated by the reproducibility of international standards. The international PDB[18] (Pee Dee Belemmitella) was used as standard to calculate $\delta^{13}C$ and $\delta^{18}O$ respectively. A negative δ value means that the isotopic ratio of the sample is lower than that of the standard. For example, a $\delta^{15}N$ value of +30‰ means that the $^{15}N/^{14}N$ of the sample is 30 parts-per-thousand or 3% higher than the $^{15}N/^{14}N$ of the 13 standard.

3 Results and Discussion

3.1 Elemental and Micromorphological Analysis

Backscattered electron photomicrographs (Figs. 1, 2) show the morphology of loose dust samples. Organic

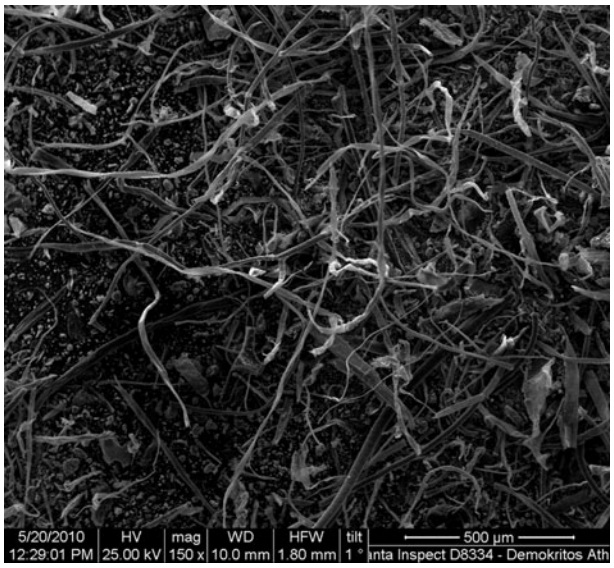

Figure 1: SEM photomicrograph (SEI images, x150) of loose dust samples, showing fibres from human hair and clothes.

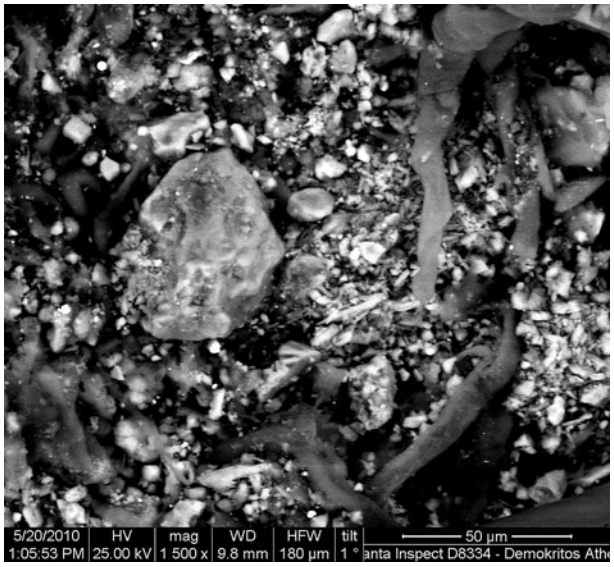

Figure 2: SEM/BSE (x1500) photo micrograph, illustrating a typical loose dust sample comprising small inorganic particles and fibrous organics.

fibres are discriminated from inorganic particles, on the basis of their relatively low mean atomic numbers. Organic fibres are likely to be derived from human hair and clothes.[19] Inorganic particles are fine, with a typical particle size of up to about 5-10 µm and they correspond to soil-mineral dust. Point EDX was performed to characterise the elements that compose mineral dust, while microscopic observations can reveal the identity of the organic fibres.

Point EDX measurements of individual particles elucidated that Ca-S and O- rich particles were the most abundant type (Fig. 3). These elements are associated with the presence of calcium sulphate, that occurs as a gypsum decay product of the limestone building material of the Archive. Particles rich in Si and O are attributed to quartz (SiO_2), whereas Fe-rich particles are likely to represent hematite (Fe_2O_3). Particles comprising Ca with C and O represent calcite that possibly occurs as a deterioration product of the fabric of the building (Fig. 4). Multicomponent particles containing Al, Si and Ca (Fig. 5) are attributed to clay-bearing or

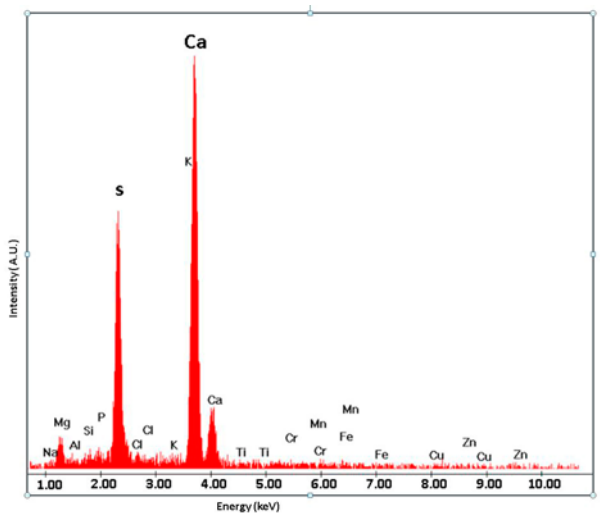

Figure 3: EDX spectrum associated with the presence of calcium sulphate.

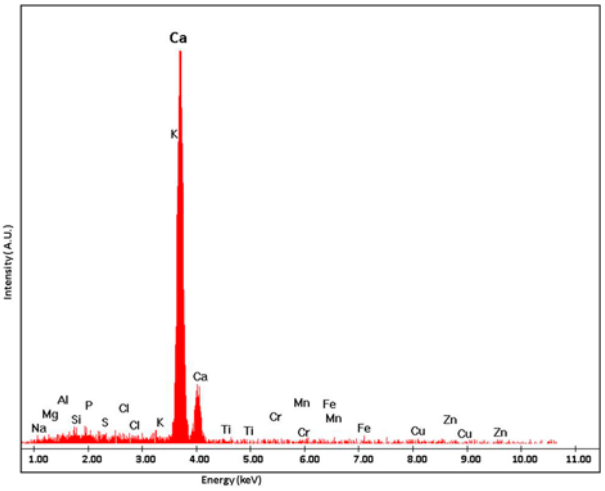

Figure 4: EDX spectrum associated with the presence of calcite.

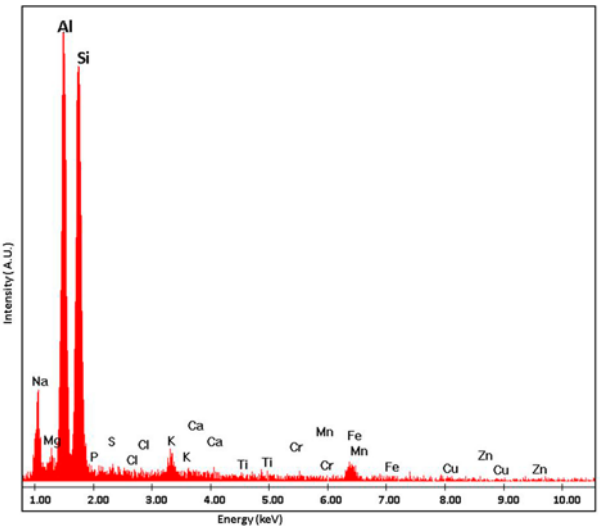

Figure 5: EDX spectrum of aluminosilicates and cements.

clay-derived materials such as Portland cement, brick dust and soil. These particles originate from building materials that are related either to the building fabric or to construction works that took place in the surrounding area of Athens city centre. Major peaks of Na and Cl reflect the presence of halite (sodium chloride,

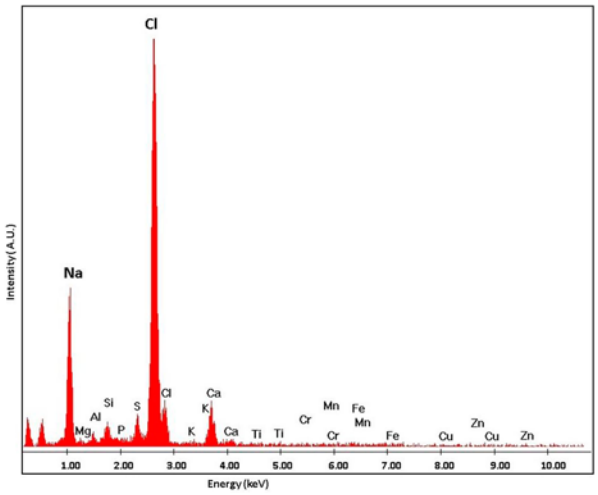

Figure 6: EDX spectrum revealing the presence of halite.

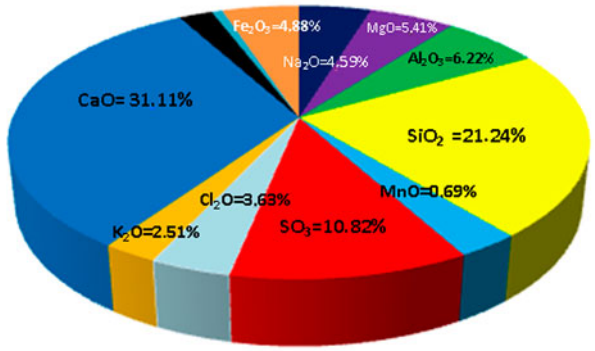

Figure 7: Bulk analysis for oxides and elements of dust samples normalized to 100%, by SEM/EDX.

NaCl; Fig. 6), potentially derived from visitors hands or sea spray since the Library is located in the center of Athens close to saline sources.

Bulk analysis results for major oxides are presented in Fig. 7. High CaO content indicate that 31% of the inorganic fraction of the loose dust is composed of calcium carbonate. Many samples have Na_2O/Cl ratios indicating that all sodium and chlorine were present as halite. Supposing the bulk of the sodium and chlorine are present as halite, then halite typically comprises 8% of the dust. The remaining fraction of dust is a mixture of quartz and aluminosilicates/clay. Calculating the approximate weight ratio of CaO to SO_3 ranges between 0.7 and 1.4, showing that the bulk of these oxides are present in the form of calcium sulphate compounds with in some cases significant amounts of calcite. The ratio of SiO_2/Al_2O_3 is estimated that equals to 2:1 in common clay products. Therefore it can be estimated that possibly half of the SiO_2 is associated with clay minerals while the remainder is present as quartz. Aluminosilicates, clay and quartz are minerals that are usually detected in soil dust that is imported in the Archive through visitor's shoes.[20-21]

3.2 Stable isotope analysis

The carbon and oxygen isotopes in dust samples were analyzed in order to evidence the carbonate origin. The isotopic value of carbonates depends mainly on the isotopic composition of atmospheric CO_2 and water and on the degree to which the isotopic equilibrium is reached and therefore the factor of fractionation of the components ($\delta^{13}C_{CaCO3}$, $\delta^{13}C_{CO2}$, $\delta^{18}O_{CO2}$ and $\delta^{18}O_{H2O}$). Isotope data of the calcite from mortar represent non isotopic equilibrium. In the study of Kosednar-Legenstein et al.,[22] it has been demonstrated that the continuous enrichment of $\delta^{13}C$ versus $\delta^{12}C$ of the calcite precipitated in the CO_2 absorption experiments is explained by a continuous enrichment of $\delta^{13}C$ relative to $\delta^{12}C$ of the gaseous CO_2 due to kinetic isotope fractionation during calcite formation. The isotopic values for C and O within the precipitation of calcite by atmospheric CO_2 absorption are using the local isotopic composition of water and atmospheric CO_2 has been detailed in previous work of Dotsika et al.[23] The isotopic values of the calcite-based dust particles comprise a wide range of $\delta^{13}C$ and $\delta^{18}O$ values, from -12 to -3.4‰ and from -7.7 to -3.2‰ (VPDB) respectively and they are plotted in Fig. 8. The isotopic composition of particulate matter (PM) is plotted in Fig. 8 (Lines 1,2,3). In the same diagram line 1 (δC^{13}< -27) represents particles that originate from industrial combustion while the lines 2 and 3 (for -26.5<$\delta^{13}C$<-25.5) represent dust particles that originate from traffic emissions.[22] In Fig. 8, area A is developed according to reference data on isotopic signature on mortar degradation and experimental results on the fractionation mechanisms of carbonate materials.[22]The isotopic signature of samples plotted in this area represent calcite based dust particles that originate from mortar weathering products. Samples plotted on area B represent isotopic values of local marine limestone in the vicinity of Athens.[22] These values correspond to samples obtained from local marine limestone (Kitheronas and Penteli) in the vicinity of the historical buildings, which was the main source of ancient raw material for burning.[23] The isotopic values for local marine limestone range between –1.4 and 2.8‰ for $\delta^{13}C$ and between –7.7 and –2.8‰ for $\delta^{18}O$ and they are plotted in area B.

According to the results of mineralogical and chemical analysis, the principal component in dust samples is calcite that occurs as a deterioration product of the building fabric. The isotopic values for limestone mortars are compared to the isotopic signature of dust particles with the view to determine any potential cor-

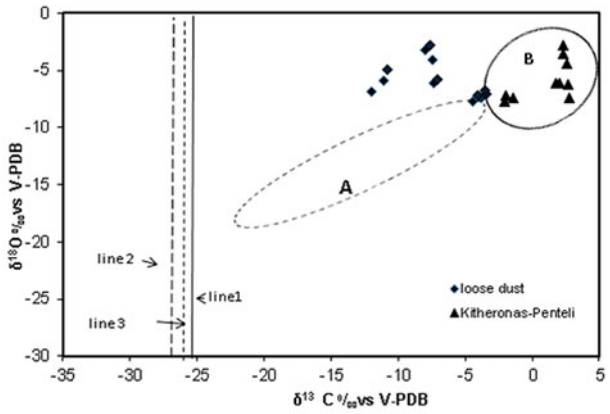

Figure 8: $\delta^{13}C$ vs. $\delta^{18}O$ values of dust samples from the Hellenic literary and historical archive; Area A: precipitated calcite formed from atmospheric CO_2 and contaminated by natural limestone Area B: Isotopic composition of local marine limestone for Kitheronas-Penteli, mountains in the vicinity of Athens. Line 1: $\delta^{13}C$< -27 (line1), particles originate from industrial combustion. Line 2: dust particles originate from traffic emissions.
Line 3: dust particles originate from traffic emissions.

relation. The location of dust samples in areas A and B demonstrate that there is a correlation between dust particles and limestone weathering products. However, the isotopic signature of dust particles follow a shift towards more negative values in $\delta^{13}C$ in comparison with limestone weathering products showing the contribution of industrial combustion which means that dust particles originate from traffic emissions (soot dust). However, $\delta^{18}O$ indicate more positive values compared with ^{18}O of mortar that is attributed to the dissolution/recrystallization processes that take place on the surface layers of the material and cause the cementation of dust particles.

4 Conclusions

A combination of analytical techniques was applied to characterize particulate matter in Hellenic Historical and Literary Archive. The results demonstrated that particulates are composed of soil dust and fibers. Soil dust is composed of limestone degradation products, salts, clays and various feldspar minerals. Fibers are likely to be derived from visitor's hair and clothes. Calcite-based dust particles are correlated with deterioration products of the building fabric, while aluminosilicates and clays possibly correspond to soil dust. Stable isotope analysis made possible to determine the sources of dust, confirming that calcite dust particles are derived from limestone weathering products and soot dust while signs of recrystallization are detected. Stable isotope analysis proved a powerful tool in dust analysis that makes possible to determine the different sources of dust and hence define its origin. The origin of dust will define the nature of mitigation strategies that need to be employed in order to eliminate the ingress of dust in the Hellenic Literary and Historic Archive.

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