Applied Geochemistry 48 (2014) 122–131

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Impact of air pollution in deterioration of carbonate building materials in Italian urban environments

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ARTICLE INFO

Article history:
Available online 15 July 2014
Editorial handling by M. Kersten

ABSTRACT

This work presents results from a petrographic, morphological and chemical study of the black crusts developing on monuments in three Italian cities, the Cathedral of Milan, the Cathedral of St. Maria del Fiore in Florence, and the Vittoriano Monument in Rome.

Black crusts (BCs) were studied with traditional techniques such as optical microscopy (OM), scanning electron microscopy coupled with energy-dispersive X-ray spectrometry (SEM-EDS) and infrared spectroscopic techniques (FT-IR), in combination with laser ablation inductively coupled mass spectrometry (LA-ICP-MS), which has shown itself to be particularly useful in determining concentrations of heavy metals in BCs.

Although the BCs of the three monuments show general enrichment in heavy metals with respect to the substrate (S), interesting differences were observed among them. The BCs from Milan are the richest in heavy metals, particularly Pb and Zn, reflecting the severe air pollution of this very large city, which, in addition to its intense traffic, is located in the most highly industrialized area of Northern Italy. The BCs from the south-eastern side of the Cathedral of St. Maria del Fiore in Florence, facing a pedestrian area, show little enrichment in heavy metals, and those from the Vittoriano Monument in Rome, which is exposed to intense road traffic, display variable enrichment, attributable to mobile emission sources.

Results show that the various enrichment trends in heavy metals observed in the BCs of these three monuments are due to many factors: various sources of anthropogenic pollution, sampling height, exposure, orientation, and the shape of the deposition surface.

1. Introduction

The recent decline in air quality, due to increasing amounts of anthropogenic pollutants released into the atmosphere of cities, has had dramatic effects on cultural heritage. Buildings and monuments in city centers are typically blackened, due to the accumulation on their surfaces of atmospheric pollutants. The formation of black crusts is often due to the growth of gypsum on calcareous substrates, particularly limestone and marble, sheltered from water and attacked by an SO_2-polluted atmosphere (Moropoulou et al., 1998).

In addition to gypsum, elemental carbon and organic carbon compounds are usually the main components of crusts (Ghedini et al., 2006).

Many studies have shown the close correlation between environmental pollution levels and the formation and development of black crusts (Ausset et al., 1996; Barca et al., 2010; Del Monte et al., 1981; Grossi et al., 2003; Rodriguez-Navarro and Sebastian, 1996; Turkington et al., 1997; Zappia et al., 1998). In particular, study of trace elements, such as heavy metals in the BCs developing on monuments, provides useful information on pollution sources (Barca et al., 2010, 2011, 2012; Belfiore et al., 2013; Comite et al., 2012; La Russa et al., 2013).

This work presents the results of a systematic mineralogical, petrographic and chemical examination of BCs and their substrates on samples from three important monuments in three cities of central-northern Italy: the Cathedral of Milan, the Cathedral of St. Maria del Fiore in Florence, and the Vittoriano Monument in Rome. They were chosen for their historical significance and because they offer the possibility of analyzing the BCs developing in three Italian cities exposed to various sources of pollution. The air quality in the city centers of Milan, Florence and Rome is known

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http://dx.doi.org/10.1016/j.apgeochem.2014.07.002
0883-2927/

to be very bad for many reasons; they are all large cities characterized by very intense traffic (buses, trucks, cars, scooters) and pollution due to domestic heating (Bonazza et al., 2005; Marcazzan et al., 2001). In addition, among the three cities, Milan has the highest level of air pollution, partly because of its position in a heavily industrialized area, with power plants, refineries, incinerators, and chemical and metallurgical factories in its hinterland (Marcazzan et al., 2001, 2003).

Several techniques were used for the study, including polarizing optical microscopy (OM), scanning electron microscopy coupled with energy-dispersive X-ray spectrometry (SEM-EDS) and Fourier transform infrared spectroscopy (FTIR), in combination with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The aim of this work was to correlate the morphological, petrographic and geochemical characteristics of the BCs on the studied monuments with the degree of air pollution, as well as the exposure and orientation of their deposition surfaces.

2. Materials and methods

2.1. Sampling

Seven BC samples were collected from the surfaces of the three monuments (figure as Supplementary material). Sampling was carried out by Bonazza et al. (2005) within the framework of the CARAMEL national research project, developed in 2003 by the Institute of Atmospheric Sciences and Climate (ISAC) of the Italian National Research Council (CNR) in Bologna. The project aimed at quantifying the carbonaceous fraction within damaged layers of historic buildings in various European cities.

In this study, three Italian cities, namely Milan, Florence and Rome, were chosen for their notoriously poor air quality, subjected as they are to considerable pollution from emissions of gases from road traffic, domestic heating and industry. In addition, the monuments in each of the above cities were chosen for their historical and artistic importance and for the stone materials used to build them (marble and limestone).

The Cathedral of Milan (14–19th centuries) is a Late Gothic building in the center of the city. It was designed by Gian Galeazzo Visconti in 1386, but work on it lasted until 1894, when the façade was completed. Milan is a very large city, with many residential and commercial buildings and intense road traffic; it also lies in the center of the Po Valley, the most highly industrialized area in Northern Italy (Marcazzan et al., 2001, 2003). The Cathedral is now in a pedestrian area (since 1969). The two BC samples studied here (DM8, DM11) were collected from the south side of the building at about 40 m from ground level. Two substrate samples of Candoglia marble were also collected.

The Cathedral of St. Maria del Fiore (13–19th centuries) is in a pedestrian area (since 2009) in the center of Florence, on the site where the Basilica of St. Reparata, built in the 5–6th centuries, once stood. The construction of the Cathedral, directed by Arnolfo di Cambio, started in 1296 and lasted for nearly five centuries, ending in 1884. Four BC samples (DF3, DF4, DF8, DF10) were taken. All samples and their Carrara marble substrates were collected from the south-eastern side of the building at a height of about 60 m from ground level. They were all collected from decorative elements, except for DF10, which was taken from a horizontal surface where the crust showed growth oriented in the direction of the prevailing wind.

The national monument built in honor of Vittorio Emanuele II of Savoy, known as the Vittoriano Monument, is located in Piazza Venezia in the center of Rome. Its construction started in 1885 under the direction of the architect Giuseppe Sacconi, and was completed in 1935. The monument is now entirely surrounded by roads carrying heavy traffic. One representative sample of black crust and the relative substrate (Botticino limestone) was collected from about 20 m from ground level (VR2). Table 1 lists all the examined BC samples, together with details of sampling location, shape of deposition surface and information about previous restoration works.

2.2. Analytical methods

Microscopic study of BCs and substrates was carried out on thin sections by polarizing optical microscopy.

Scanning electron microscopy coupled with energy-dispersive X-ray spectrometry (SEM-EDS) analyses gave information on BC micromorphology and chemical composition (major elements). Analyses were performed on a Tescan Vega LMU scanning electron microscope equipped with EDAX Neptune XM4 60 microanalysis working in energy dispersive spectrometry, with an ultrathin Be window to ensure lower detection limits (to the order of 0.1%) for all elements analyzed. Operating conditions were set at 20 kV 138 accelerating voltage, 0.2 mA beam current, 100 s acquisition time, and 30–35% dead time. Precision was better than 1% for major elements and better than 3% for minor elements. Accuracy was of the same order of magnitude as precision.

FT-IR was used to identify the mineralogical phases of damaged layers. A Perkin Elmer Spectrum 100 spectrophotometer was used, equipped with an attenuated total reflectance (ATR) accessory. Infrared spectra were recorded in ATR mode, range 500–4000 cm^{-1} at a resolution of 4 cm^{-1}.

To determine trace element concentrations, the samples were analyzed by LA-ICP-MS on an ElanDRCe (Perkin Elmer/SCIEX), connected to a New Wave UP213 solid-state Nd-YAG laser probe (213 nm). Analytical procedures for acquisition of LA-ICP-MS data were those tested in the Mass Spectroscopy Laboratory, DiBEST, University of Calabria (Barca et al., 2010, 2011). After analytical sequencing, the data were transmitted to a PC and processed by the GLITTER program (van Achterberg et al., 2001). Constant laser repetition rate was 10 Hz and fluence about 20 J/cm^2. Each ablation

Table 1
List of the black crust samples and description of the sampling points (from Bonazza et al., 2005).

Sample	Height (m)	BC typology	Shape of deposition surface	Sampling location	Past restoration work
Milan Cathedral					
DM8	40	Dendritic	Horizontal surface, from a decorative element	South side	None during the last 500 years
DM11	40	Dendritic	Concave surface, from a decorative element	South side	
St. Maria del Fiore Cathedral in Florence					
DF3	60	Dendritic	Vertical surface, from a decorative element	South-east side	1500
DF4	60	Dendritic	Horizontal surface, from a decorative element	South-east side	
DF8	60	Dendritic	Horizontal surface, from a decorative element	South-east side	
DF10	60	Dendritic	Horizontal surface, from a decorative element	South-east side	
Vittoriano Monument in Rome					
VR2	20	Compact	Horizontal surface, from the basis of a column	North side from right propylea	None prior to sampling