Correlation between black crust formation on limestone monuments and the urban pollution

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Air pollution is an historic concern and is mentioned since Antiquity. However, measurements are relatively recent and ancient data on atmospheric pollution are scarce, punctual and often incomplete. In a geological context, proxies can be used, such as ice cores, lacustrine sediments or peat bogs to give information on the past environment. The aim of this project is to propose a new proxy: the black crusts formed on limestone monuments. In sheltered zones of monuments, thick black crusts result from a sulfation reaction, during which SO_2 reacts with calcite to form gypsum ($CaSO_4 \cdot 2H_2O$) and from the entrapment of particles and especially soot, causing its blackening. They have thus recorded the atmospheric pollution and its evolution through the centuries or decades. However, this requires to constrain the formation of black crusts as a function of the environment. For that, we have studied two kinds of system. First, limestone samples (as well as marble and modern glass) have been exposed for 1 year in 25 different European sites (traffic, urban, rural) in order to link the composition of a stratum to the atmospheric composition and to determine the formation rate. Samples were characterized by spectrophotometry (reflectance R and chromaticity ΔE^*_{ab}), optical and Scanning Electron Microscopy – Energy Dispersive Spectrometry (SEM-EDS) (particles), X-Ray Diffraction (XRD) and Raman spectroscopy (mineralogy), Ion Chromatography (sulfates, nitrates, etc.) and Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) (trace metals). Results have shown significant differences of the black crust composition as a function of the surrounding environment and, by comparison with glass and marble samples, as a function of the material reactivity. Second, we have studied different black crust samples collected in the Père-Lachaise cemetery, of various ages (dating from 1850 until today) using similar techniques and correlated these data to measurements from Airparif in order to extend this correlation on longer times. These first results are promising to propose a novel methodology based on the use of black crusts as a proxy for the air pollution history.