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The understanding of black crust formation mechanisms to use them as an archive of the past air pollution

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Although Hippocrates or Horace wrote about air pollution in ancient times, its monitoring is relatively recent, notably by the Air Quality Network since the 1950s. New proxies are needed to understand past air pollution. Ice or sediment cores have been used to trace gases or trace metals, but they are not specific to the urban medium. Here we propose to study black crusts formed on the surface of carbonate monuments as a potential archive. These black crusts are caused by the formation of gypsum, which traps atmospheric particulate matter. As they form in areas sheltered from rain, the gypsum and deposits accumulate and can be studied as a stratigraphy. However, before analysing various tracers (such as particles, trace metals, etc.), it is necessary to determine the mechanism of gypsum growth. Two main processes have been proposed in the literature: (1) the replacement of calcite by gypsum by a sulfation reaction (by pseudomorphosis) or (2) the formation of gypsum at the outer surface by the reaction of Ca^{2+} with SO_4^{2-} in the water film. The first involves inward growth of gypsum, whereas the second involves outward growth in the same direction as particle deposition. To determine the mechanisms involved, an experiment was designed to weather ancient black crusts (~200 years old) at 100% relative humidity in the presence of ozone and ^{34}S-labelled SO_2. The nanoSIMS images showed that areas of ^{34}S-enriched gypsum are located on the outer surface of the existing black crust. This shows that gypsum formation is outwardly directed, similar to particle deposition, which is consistent with other parallel observations (detachment, morphology, particle stratigraphy). If the gypsum integrated the particles as it formed, this strengthens the preservation of the black crust stratigraphy and the interpretation of trace metal profiles in black crusts as evidence for the evolution of pollution sources through time.