A step towards the understanding of metal-catalysed degradation of marble by outdoor pollution

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The role of metal-based catalysts is fundamental for promoting various organic transformations towards strategic compounds. What is less well known is the involvement of metal-mediated catalysis in the undesirable degradation of stone materials by atmospheric pollution. Metals embedded in atmospheric particulate matter (PM) as oxides and salts, in fact, seem to play a catalytic role in the sulphation of carbonate materials (i.e. marble) thus representing a serious threat for cultural heritage. The typical weathering process involves the conversion of atmospheric SO_2 (produced by combustion of fossil fuels), in presence of H_2O, into H_2SO_4 followed by reaction with $CaCO_3$. This leads to the formation of *black crusts*, which are composed of $CaSO_4 \cdot 2H_2O$ (gypsum) inside which PM is embedded. In order to better preserve the exposed monumental surfaces over time, a continuous study is fundamental aimed at disentangling the mechanism of *black crusts* formation and, specifically, the role of metals. According to our preliminary studies, aqueous solutions of various metal salts and oxides (namely, Fe_2O_3, $Fe(NO_3)_3 \cdot 9H_2O$, $CuCl_2 \cdot 2H_2O$, $MnCl_2 \cdot 4H_2O$, $PbCl_2$, Cr_2O_3, V_2O_5), mixed with graphitic carbon which simulates the elemental carbon present in PM, were prepared at determined concentrations. The solutions concentration was calculated based on the data from urban particulate matter (PM 2.5 sampled on filters in the city of Milan [1]) and the choice of those specific metals was done according to previous literature studies [2, 3]. In addition, solutions composed of mixtures containing some metals or all of them together were also prepared to be deposited on the marble samples ("white Carrara"). Specifically, three mixtures were considered in order to evaluate a potential synergistic effect among metals: the first one containing Fe^{3+}, Cu^{2+}, V^{5+}; the second one containing Fe^{3+}, Mn^{2+}, Pb^{2+}, Cr^{3+} and the third one containing all the selected metal cations. The solutions were properly deposited on the surface of a number of marble samples. Moreover, the same PM 2.5 extracted from Milan air sampling filters was also deposited on samples serving as a reference and all the samples were compared to untreated marble specimens ('blank'). Finally, the samples were put inside climate chambers for accelerated aging over four weeks long. The chambers were two: the first chamber ("corrosion chamber") supplying SO_2 and humidity at selected concentration and temperature; the second one ("light radiation chamber") simulating the sunlight irradiation naturally falling on monumental stone during the day. To the best of our knowledge, this experimental combination is particularly innovative as never used before. This first phase of experimentation has highlighted the complexity of the sulphation process since no univocal evidence on the role of specific metals was exhaustively achieved. Nevertheless, some specific metals seemed to be faster than others in promoting the catalytic process and the metal mixtures displayed a synergistic action on gypsum formation. Hence, some conclusive considerations could be drawn as the first step towards the understanding of metal-catalysed degradation of marble by outdoor pollution. The final scope is the creation of a mathematical model able to predict *black crusts* formation for a given site of cultural interest in relation to atmospheric pollution. In fact, this research work is part of the interdepartmental SEED 2019 project of the University of Milan entitled SciCult.

References

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