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Anthropogenic salts from deteriorated stones of a historical monument (Kraków, Poland)

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The results focus on the stone architectonic elements of the Hebdowski Palace in the Okół, an old, medieval part of Kraków. The object was built around 1400, then rebuilt at the turn of the 17th century and at the first half of the 19th century. Its façade was covered with plaster, whose scaling fragments prior to the renovation in 2015 revealed underneath bricks, particularly in the lower part of the palace. The sandstone elements were used in the main portal, while the limestone ones in window frames of the lower section of the façade, base mouldings, and the buttresses at the corner of Poselska and Senacka streets (one of the oldest streets in Kraków). The stone blocks show various forms of damage, ranging from the accumulation of black crusts and efflorescences to crumbling and scaling of their surfaces. Optical microscopy, scanning electron microscopy (SEM-EDS), micro-Raman spectroscopy and X-ray diffractometry (XRD) were used for analysing deterioration products of the stone samples that were collected during the restoration campaign of 2015.
The salt minerals detected in the efflorescences and the black crusts include mainly gypsum $CaSO4•2H_2O$ and halite NaCl. On the surface of the limestone gypsum is accompanied by oxalates (whewellite $CaC2O4•H_2O$ and/or weddellite $CaC2O4•2H_2O$). The black crust developed on both stone types also contain numerous dust particles and a carbonaceous matter, probably soot.
The origin of the anthropogenic salts can be mainly assigned to air pollution, to the stones themselves (mainly in the case of the limestone), and to migration of ions from some elements of the façade (e.g. plaster) in the case of the sandstone. The chemicals used for removing ice from streets and pavements (chiefly NaCl and CaCl2) also seem to be important in the formations of the salts. Finally, the existence of simple life forms, such as lichens and fungi, could result in the precipitation of oxalates.

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