Black, anthropogenic, manganese-rich crusts on the Freiburg Minster

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Black, Mn-rich crusts observed on the Freiburg Minster's facade, Germany, were measured in-situ by portable XRF. The XRF was calibrated by a procedure developed for this purpose, to obtain results in absolute surface densities. The black crusts on the minster's facade resemble rock varnish crusts, which can be found worldwide, and have been content of intensive investigations since more than 200 years. In addition, 200-nm fs LA-ICP-MS and STXM-NEXAFS measurements, Raman scattering, and imaging microscopy were performed, to obtain further insight into the crusts, such as biogenic contribution, element distribution, trace element composition, and available functional groups. While Mn-rich crusts (Mn >150 µg cm^{-2}) were restricted to a maximum height of about 7 m, crusts containing biogenic encrustations, gypsum, and soot, covered the minster's facade up to at least 30 m height. An exception were crusts with a surface density of 1360 µg cm^{-2} Mn, that developed on the Renaissance portico (~7.7 m height) within a period of only 12 years. These crusts revealed an accumulation rate of >100 µg cm^{-2} a^{-1} Mn. Trace element analyses support the theory that vehicle emissions are responsible for most of the Mn supply. Pb, Ba, and Zn correlate with Mn, indicating element sources such as tire material, brake pads, and resuspended road dust. Microscopical investigations showed no organisms on the Mn-rich crusts, however, black, Mn-free crusts sampled at greater heights (>8 m) exhibited fungal and cyanobacterial encrustation. C-rich material, displaying NEXAFS and Raman signatures of soot-like material, was found in the vicinity of the black Mn-rich crusts. Our results suggest that the crusts develop abiogenically, with vehicle emissions as dominant element sources.