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Black manganese-rich crusts on a Gothic cathedral

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ABSTRACT

Black manganese-rich crusts are found worldwide on the façades of historical buildings. In this study, they were studied exemplarily on the façade of the Freiburger Münster (Freiburg Minster), Germany, and measured in-situ by portable X-ray fluorescence (XRF). The XRF was calibrated to allow the conversion from apparent mass fractions to Mn surface density (Mn mass per area), to compensate for the fact that portable XRF mass fraction measurements from thin layers violate the assumption of a homogeneous measurement volume. Additionally, 200-nm femtosecond laser ablation-inductively coupled plasma-mass spectrometry (fs LA-ICP-MS) measurements, scanning transmission X-ray microscopy-near edge X-ray absorption fine structure spectroscopy (STXM-NEXAFS), Raman spectroscopy, and imaging by light microscopy were conducted to obtain further insight into the crust material, such as potential biogenic contributions, element distributions, trace element compositions, and organic functional groups.

While black crusts of various types are present at many places on the minster's facade, crusts rich in Mn (with a Mn surface density > 150 μg cm^{-2}) are restricted to a maximum height of about 7 m. The only exceptions are those developed on the Renaissance-Vorhalle (Renaissance Portico) at a height of about 8 m. This part of the façade had been cleaned and treated with a silicon resin as recently as 2003. These crusts thus accumulated over a period of only 12 years. Yet, they are exceptionally Mn-rich with a surface density of 1200 μg cm^{-2}, and therefore require an accumulation rate of about 100 μg cm^{-2} Mn per year.

Trace element analyses support the theory that vehicle emissions are responsible for most of the Mn supply. Lead, barium, and zinc correlate with manganese, indicating that tire material, brake pads, and resuspended road dust are likely to be the element sources. Microscopic investigations show no organisms on or in the Mn-rich crusts. In contrast, Mn-free black crusts sampled at greater heights (> 8 m) exhibited fungal and cyanobacterial encrustation. Carbon-rich spots were found by STXM-NEXAFS underneath one of the Mn-rich crusts. However, these carbon occurrences originate from soot and polycyclic aromatic hydrocarbons (PAHs) deposited on top of the crust, rather than from organisms responsible for the crust's formation, as shown by STXM-NEXAFS and Raman spectroscopic measurements. Our results suggest that the crusts develop abiogenically, with vehicle emissions as dominant element sources.

1. Introduction

Historic buildings and monuments in urban areas often show extensive dark or black discolorations, which affect their aesthetic appeal and whose restoration can have considerable economic implications (Newby et al., 1991). Until recently, most of these blackened areas were thought to be formed by the accumulation of soot, which on carbonate building materials is often incorporated into a matrix of gypsum. The main source of the soot can be traced back to fossil fuel combustion, which depending on the time and place concerned may be dominated

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by coal burning, diesel engines, and other activities (Bonazza et al., 2005, 2007a; Brimblecombe and Grossi, 2009; De Oliveira et al., 2011; Grossi and Brimblecombe, 2002, 2008; Pio et al., 1998; Ruffolo et al., 2015; Sáiz-Jiménez and Hermosin, 2004).

The gypsum layer develops as a result of the sulfur dioxide (SO_2) released in the course of fossil fuel combustion, which can either react directly with the carbonate material or after its oxidation to sulfuric acid in the atmosphere (Bonazza et al., 2005; Brimblecombe and Grossi, 2009; Grossi and Brimblecombe, 2002; Ruffolo et al., 2015). Colored organic compounds incorporated into the coatings can result in brownish or yellowish discolorations (Bonazza et al., 2007a; Brimblecombe and Grossi, 2009; Grossi and Brimblecombe, 2008). More recently, the growth of cyanobacteria (Bonazza et al., 2007b; Uchida et al., 2016), bacteria (Miller et al., 2012), and fungi (De Oliveira et al., 2011; Gorbushina et al., 1993; Saiz-Jimenez et al., 2012; Viles and Gorbushina, 2003) was also implicated in the discoloration of exposed stone materials.

However, in the last few years it was discovered that some black crusts on buildings in urban open areas are actually Mn-rich coatings (Grissom et al., 2014; Grüner et al., 2011; Livingston et al., 2016; Uchida et al., 2016; Vicenzi et al., 2016) with an as yet unknown genesis. These black crusts lack identifiable biogenic structures (Grissom et al., 2014; Livingston et al., 2016; Vicenzi et al., 2016) and are thus dissimilar to Mn-rich crusts found in cave environments, which had often been found to be of biogenic origin (Frierdich et al., 2011; Miller et al., 2012; Saiz-Jimenez et al., 2012; White et al., 2009). Manganese-rich coatings on facades of buildings of historical interest are often present on siliceous stones, such as quartz-based sandstones, in contrast to the soot-rich crusts on limestones, marbles, or calcareous sandstones (Bonazza et al., 2005, 2007a; Brimblecombe and Grossi, 2009; Grossi and Brimblecombe, 2002, 2008). Grossi and Brimblecombe (2002) report that quartz-based sandstones behave differently from limestones and marbles, since they are resistant to sulfur-based acids in the air and they "tend to become dirtier in rain-washed areas than in sheltered areas".

Such Mn-rich coatings were described from the Freiburger Münster, Freiburg, Germany (Fig. 1) by Grüner et al. (2011). They had also been observed on several other buildings of historical interest, such as at the church in Stödtlen, Germany (Grüner et al., 2011), the Smithsonian Institute in Washington D.C., USA (Grissom et al., 2014; Livingston et al., 2016; Vicenzi et al., 2016), and the Khmer temples in Cambodia (Uchida et al., 2016), indicating the worldwide abundance of these crusts. Manganese-rich crusts on historical buildings are not only found on sandstone building blocks, but also on laterites and bricks (Uchida et al., 2016). No systematic association has been observed between the surface roughness of the building blocks and crust development, neither on the Freiburger Münster, nor on the Smithsonian Castle (Vicenzi et al., 2016). Furthermore, the patches are most abundant on the building blocks themselves, and only to a lesser extent on the mortar between them. The crusts seem to start growing on the sandstone and only cover the mortar in cases when the crusts span several blocks, an observation also made at the Smithsonian Institute (Vicenzi et al., 2016).

As these patches disfigure the appearance of the buildings, attempts were sometimes made to seal and protect the building blocks by painting them with various coatings or sealants. At the Freiburger Münster manganese-rich crusts had been found especially prominently on the Renaissance-Vorhalle built in 1620. This addition to the minster was treated with a hydrophobic, diffusion-open silicon resin paint during restoration work in 2003 (Grüner et al., 2011), which ironically might have created conditions particularly suitable for Mn-crust growth. Another part of the minster, the Schöpfungsportal (creation portal), was treated with a pore-closing silicic acid ester on several areas. Black crusts grew at these locations within only about four years. The Schöpfungsportal is of specific interest because of existing photographic documentation spanning the last 100 years. It appears that the applied coatings have actually facilitated the growth of the black crusts, hence it is of importance to understand their genesis and formation mechanisms before considering further restoration measures.

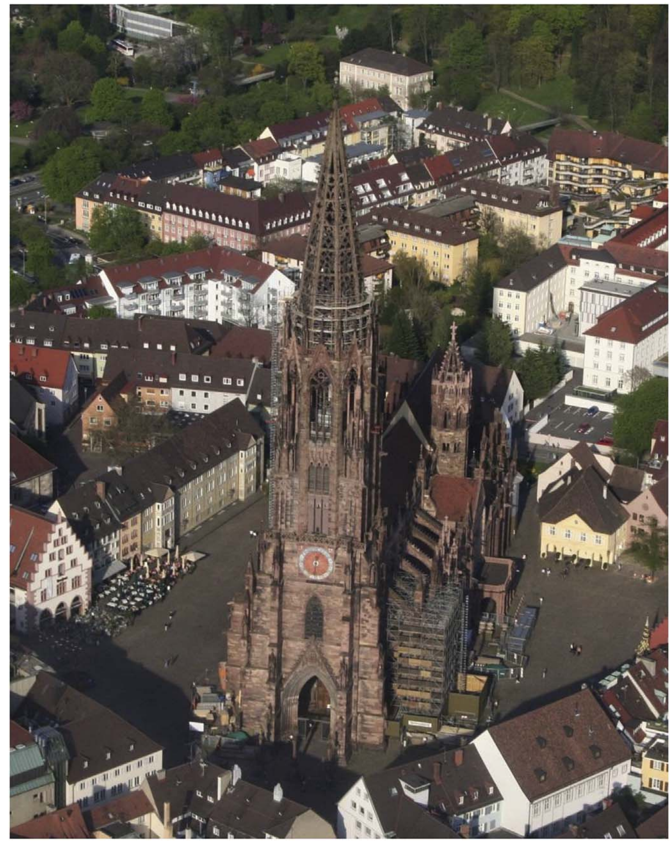

Fig. 1. The Freiburger Münster (Freiburg Minster), Freiburg, Germany. The minster, which was built from around 1200 to 1513, is a well-known cathedral belonging to the Freiburg archdiocese. (Image credit: Von Oberth, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=1158443).

This study aims to investigate the chemical composition of these coatings, which belong into the category Type IV of rock varnish (Macholdt et al., 2017), their distribution on the cathedral surfaces, their formation mechanisms, and the source of the Mn at the example of the Freiburger Münster. The minster, which was built from around 1200 until 1513, is a well-known cathedral belonging to the Freiburg archdiocese. Black crusts at the minster were investigated and mapped up to a height of about 30 m together with their chemical composition obtained using a portable XRF, a non-destructive technique that is very suitable for historic buildings and artefacts. In addition, we investigated two samples by optical microscopy, 200-nm fs LA-ICP-MS, Raman spectroscopy, and STXM-NEXAFS, to obtain major and trace element compositions, reveal structures, determine the presence of organisms, and investigate organic functional groups and carbon abundances within the crusts.

2. Material and methods

The Freiburger Münster was investigated at different sites and heights (Fig. 2). Measurements were taken at the Joch 12 S at the Chor (0.5 m height), at the Sterngalerie-Nische south-side (1.5 m height), below the Renaissance-Vorhalle (no silicone resin paint, about 1.5 m height), and at the Schöpfungsportal north-side (2 m height), at the south/east Facade of the "Sterngalerie am Hauptturm" (1.5 m height), at the pillar located at 2/3 on the north-side Sockelbereich (1.5 m height), at the Strebepfeiler 13/14 S (7 m height), at the Renaissance-Vorhalle (south-side) on the gallery (about 7.7 m height), at the