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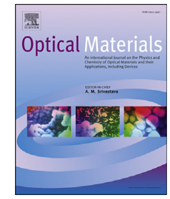

Copper-based opaque red glasses – Understanding the colouring mechanism of copper nanoparticles in archaeological glass samples

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ABSTRACT

Red opaque glasses of two different sites in central Germany, a medieval glassworks in Glashütten, Taunus Mountains, and an early modern glassworks in Wieda, Harz Mountains, were analysed with regard to their optical appearance. By scanning electron microscopy and X-ray diffraction, metallic copper nanoparticles were identified as a conspicuous constituent in these glasses. In addition, similar opaque red glasses were reproduced in the laboratory in order to better understand the manufacturing process. Detailed analysis of the optical scattering was conducted in order to evaluate the role of Cu^0 nanoparticles in the colouring mechanism relative to other possible reasons of colouration.

We find clear differences between the possible contributions of Cu_2O (cuprite) particles and metallic copper (Cu^0) nanoparticles. Through simulated backscattering spectra we were able to calculate an average copper particle radius in the archaeological glass samples resulting in a value of up to 95 nm, which matches well the results of SEM investigation (minimum 65 nm). Using the methods we applied in this study, it becomes possible to reconstruct various processing conditions as they were applied in medieval manufacture of these particular materials.

1. Introduction

One of the very first colouring agents which were applied in early glass manufacture is a red dye based on copper, dated to the 15th century BCE [1]. Starting in that time, the number of red-coloured glass artefacts produced until today has increased in countless variants. The underlying mechanism of colouring, however, has become a subject of controversy. In his seminal book on glass colouration, in 1951, Weyl described four different types of copper-based reds, either opaque or transparent, all based on metallic particles [2]. In spite of this, as discussed within the same book, other authors assumed cuprite (Cu_2O) to be the main colouring agent. According to their assumptions, the native red colour of crystalline cuprite gives rise to the appearance of many opaque red glasses (e.g. [3]). Since then, numerous articles have been published, usually following one of the two theories [4–7]. Today we know that either view can be correct in its own right, depending on the glass system and the fabrication process [8,9]: Whereas copper nanoparticles are found in glasses with low amounts of copper and lead oxide, cuprite can precipitate in high-copper-high-lead glasses and leads to a lighter red (often described as 'sealing wax' [9]) to orange colouration. Due to differences in crystal structure, chemistry and morphology the nanoparticles can be distinguished by combining X-ray diffraction and SEM techniques [9,10].

Chemically, the formation of metallic copper nanoparticles in glass matrices was investigated in several studies, usually focusing on particle size and the rules of Ostwald ripening at various temperatures between 500 °C and 800 °C [11–13]. In contrast, the formation of cuprite particles is less investigated; however, it is known from comparable glass systems that cuprite can form at temperatures above 700 °C [14]. In the present context, it should be noted that most of these studies focused on qualitative and quantitative analysis of the particles and did not attempt to correlate the number and type of the observed particles with the visual

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appearance of their samples.

We now emphasise the difference of interaction between copper nanoparticles and light of specific energies. By solving the Maxwell equations for spherical objects, Mie theory can be used to calculate the backscattering and absorption efficiency factors of particles within the size of visible light wavelengths [15]. The absorption and scattering of nanoparticles of different compositions (e.g. metallic copper or Cu_2O) can be compared to such Mie simulations of the respective optical reflectance spectra. This allows estimating the effect of particle radii in the different samples. Even though Mie theory is fundamentally based on a spherical geometry of the particles, it can be applied in a good approximation to bulk particles.

As a major advantage, optical spectroscopy is a non-destructive technique and therefore is very suitable for the study of archaeological glass samples. When combining this approach with conventional studies on nanoparticle growth in glasses, new insights can be generated using relevant processing parameters of ancient technologies. Vice versa, the same knowledge can also be transferred to modern materials [16].

The archaeological glass fragments of this study originate from two different workshops in central Germany. They were selected because of the unusual abundance of such opaque red samples at these sites. For a more detailed understanding of the manufacturing process and as a reference, we will compare archaeological opaque red glass samples with laboratory-made model glasses.

1.1. Workshop ‘Unterhalb Dornsweg’, Glashütten/Taunus, Germany (15th century CE)

A large selection of red glass samples originate from a glassworks in the Taunus Mountains, Germany, dated to the mid-15th century CE. The excavation of the experimental workshop ‘Unterhalb Dornsweg’ in 2001–2005 revealed more than 25 kg of opaque red glass shards, vessel fragments and production residuals [17]. The broad variation of forms and manufacture techniques indicate a focus on high quality glass, presumably for the upper classes. Since the main kiln of the site was destroyed completely, it is assumed that the workshop was closed either for a renewal or as a consequence of a violent dispute. In any case, it was never rebuilt [17,18].

1.2. Weinglashütte Wieda/Harz, Germany (17th century CE)

A second group of glass samples originates from a Weinglashütte (winery glass works) in Wieda, Harz Mountains, Germany, with a documented period of productivity from 1608-1623 CE. It was excavated by the ‘Archäologische Arbeitsgemeinschaft Wieda’ between 1965 and 1979 as an important regional site of manufacture in its time and a good example of the extreme diversity of glass manufacture in that period. Diverse kinds of glassy vessel fragments of many colours were excavated, among them opaque red shards coloured with copper. Flat glass manufacture is documented in addition to container glass production. The glass manufacture was most likely stopped by hazards imposed by the 30-years war [19].

2. Materials and methods

2.1. Archaeological glass samples

The red glass samples from Glashütten, Taunus Mountains (‘Unterhalb Dornsweg’) show a broad variety of colour tones ranging from purple-red over red to brown. The hue differs also within the sample between surface and bulk. The latter can be observed at broken edges of the fragments. Some samples appear to be fully opacified (Fig. 1a – c), while other samples are partially transparent (Fig. 1d).

The Wieda glass samples appear more homogeneous. Most of the glasses have a dark-red, wine coloured appearance, sometimes shifted to almost black (Fig. 2a). While some glass fragments display only applications of red decorations on otherwise colourless glass samples (Fig. 2c), others are fully composed of opaque red bulk glass. Of special interest within the feature is a group of dichroic glass fragments, showing a red appearance in reflection, but appearing blue when looked upon in transmission (Fig. 2d).

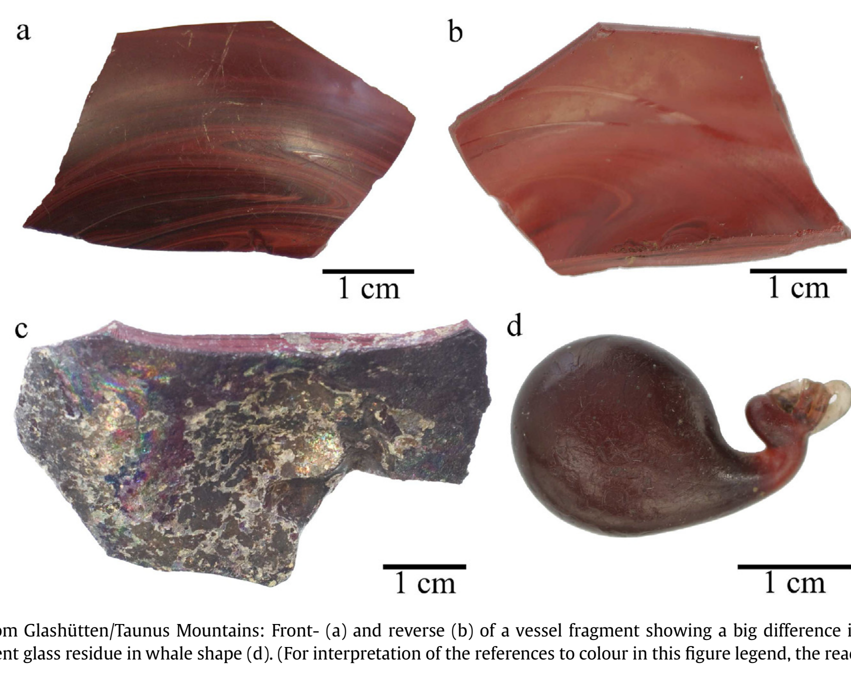

Fig. 1. Selected glass samples from Glashütten/Taunus Mountains: Front- (a) and reverse (b) of a vessel fragment showing a big difference in colour; a strongly corroded glass fragment (c); a partially transparent glass residue in whale shape (d). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)