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Technology, production and chronology of red window glass in the medieval period – rediscovery of a lost technology

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ABSTRACT

SEM-EDXA of 132 examples of medieval red window glass reveals the presence of around 1% copper oxide in all cases. SEM and TEM of selected samples confirm the presence of Cu nanoparticles. Two structural categories of red glass sheet are identified. Sheets comprising a single layer of red glass from a few tens to around 300 μm thick overlying a supporting substrate of white glass, with or without a protective cover of white glass, are typically found from the fourteenth century onwards. However, in 12th–14th century England, France and Spain, and perhaps elsewhere, typical red glass sheets have a complex microstructure comprising multiple coloured striae about 1 μm thick in a white background. SEM–EDXA, TEM and LA-ICP-MS have been used to characterise and investigate the technologies of the two types in detail. The single-layered glasses were produced using an approach analogous to that of copper red glass in the modern period, where a red glass is flashed onto a colourless base. In contrast, the multi-layered glasses were formed by the incomplete mixing of an oxidised high-Cu and a reduced low-Cu glass. The red colour forms due to the diffusion of oxidised copper into the reduced glass and the nucleation and growth of metallic copper during heat-treatment. This represents a previously unrecognised medieval glass technology, where red was created by mixing two weakly coloured glasses, a complex, arcane and mysterious procedure which must have reinforced the exclusivity of the craft. The occurrence of the technique has implications for dating windows and the identification of glass which has been inserted in early restorations and repairs, for the trade in coloured glass and for the transfer of glassmaking technologies in medieval times. It provides a link between stained glass window technology of the high medieval period and the glass-colouring practices of the late first millennium CE.

1. Introduction

Stained glass constitutes one of the most characteristic features of medieval church architecture and is an important source of medieval imagery. With origins in the first millennium AD (Cramp, 2001; Goll, 2001; Whitehouse, 2001 and other papers in Dell'Acqua and Silva, 2001) figurative glazing with coloured glass spread across much of Europe in the 12th century. Shaped pieces of coloured glass were joined with H-section lead *cames* to create representations of religious scenes or simpler, non-figurative panels which enhanced the spiritual experience by filling the building with light and colour.

Translucent red constituted an important component of the medieval glazier's palette (Fig. 1) and is one of a number of distinctively medieval technologies in the manufacture of glass windows, which include silver stain and grisaille painting. However, the manufacturing processes used to produce these *ruby red* glasses represent some of the least well understood aspects of medieval glass technology. With the exception of a rare group of late Roman glass vessels, of which the Lycurgus Cup is the best known (Barber and Freestone, 1990), virtually all known examples of earlier red glass are opaque (Freestone, 1987; Brill and Cahill, 1988; Brun et al., 1991; Freestone et al., 2003; Barber et al., 2009; Verità and Santopadre, 2010); the routine production of translucent red glass was a medieval European achievement. Furthermore, the scale of production was huge: Wedepohl (2003, 2010) has estimated that in Central Europe alone, some 40 000 tonnes of glass

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Fig. 1. Panel 8e from the Great East Window (1405–1408) at York Minster, showing the Army of the Horsemen, described in Revelations ix: 16–19 (Photograph the York Glaziers Trust, reproduced courtesy of the Chapter of York).

were produced between A.D. 1250 and 1500, and a significant part of this production was window glass. Translucent red constituted a significant element of that production, as may be seen from the surviving examples in medieval cathedrals.

The detailed mechanisms of production of red colour in medieval glass are not well understood. However, there is a consensus among modern investigators that ruby red colouration in medieval window glass is due to the presence of nanoparticles of metallic copper (Knowles, 1927; Nakai et al., 1999; Fredrickx, 2004; Farges et al., 2006; Colomban et al., 2009). The transmission of light by such glasses is low and, in the thickness of a typical window pane, they appear dark or opaque. To obtain a translucent ruby colour, all known medieval translucent reds, as well as many modern translucent red glasses, comprise at least two layers, where a thin layer of red glass is laid over a thick supporting layer of colourless or weakly coloured glass. Following art-historical convention, we will use the term "white" to encompass the range of colourless and unintentionally very pale blue, green and yellow glasses that form the substrate or support.

In the modern world, red window glass has conventionally been produced by a glass-working technique known as flashing, where a gather of molten white glass is taken on the end of a blowing iron then dipped into a pot of a colour (or vice versa). The composite gather is then blown into a cylinder of glass with a thin layer of colour on one surface. The expansion of surface area as the glass is blown can result in the development of a very thin coloured layer over a sheet of glass just a few millimetres thick. The layered glass cylinder is then cut and opened up while hot to form a flat sheet of coloured glass.

Copper may exist in glass as cuprous ions (Cu^{+}), which are virtually colourless, and as cupric ions (Cu^{2+}), which typically produce a pale blue or green colour, dependent upon the composition of the glass matrix (Weyl, 1951). The equilibrium between them, hence the colour of the glass, is controlled by the partial pressure of oxygen:

$$2Cu^{+} + O_2 = 2Cu^{2+} + O^{2-} \quad (1)$$

Oxidising conditions favour the blue-green colour. When conditions are sufficiently reducing, however, copper metal may form and, as its solubility is low, it will precipitate from the glass: