



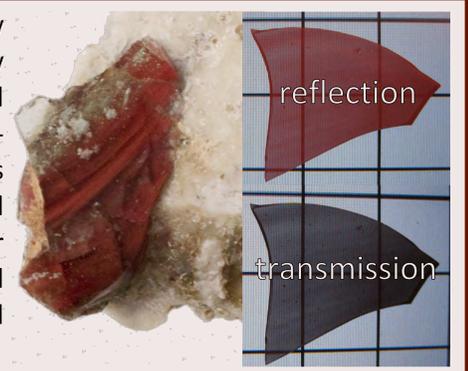
What causes the colour in Cu-red opaque artifacts?

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Since early antiquity glasses and glazes are coloured red by copper compounds - and since antiquity these glasses show very broad varieties of red. Today we know, that the red colour is formed by metallic copper nanoparticles, based on plasmon resonance interaction with the light. However, until now we do not know, why some of the red glasses are opaque, while others are transparent copper-ruby. In this study we invite you to take a look into our thoughts upon the opacity of some glass samples from medieval to modern times forest glass workshops in central Germany [1]. We combined UV/Vis absorption and reflectance data with computational spectra of glasses containing copper and/or cuprite nanoparticles and compared the obtained data with Scanning electron microscopy (SEM) and X-ray diffraction patterns. Surprisingly, we did not find the expected particles via SEM, but discovered instead phase-separation-like structures, leading to a completely new idea of Medieval opacification.



The excavation of a glassworks from the 15th ct. CE ("Unterhalb Dornsweg", Taunus, Germany) in 2001 revealed uncountable fragments of opaque red glass. This workshop apparently experimented on these opaque red glass samples [1,2]; the fabrication site was closed after a violent incident and not rebuilt; the reason for this incident remains unknown. The dichroic flashed glass sample is from a glassworks in Wieda, Germany (17th ct. CE) and was included in this study, since the semitransparent samples allow the use of optical spectroscopy and thus help understanding the role of copper in the glass [3].

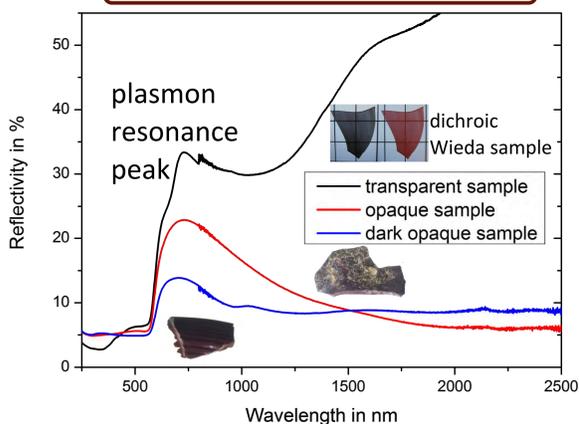


Composition in wt-%	SEM-EDS	XRF
SiO ₂	54.9	53.6
P ₂ O ₅	2.9	4.6
Al ₂ O ₃	2.9	2.9
MgO	3.9	5.1
CaO	23.7	23.2
Na ₂ O	2.2	3.8
K ₂ O	3.0	3.0
Cu ₂ O	2.3	1.1
Σ	95.8	96.9

A very surprising fact was the high viscosity of the Medieval glass. To understand the behavior of the material, a model glass with comparable composition was prepared. The red colour of the glass could only be achieved under strongly reducing conditions, while without reducing agents the glass remained blue.

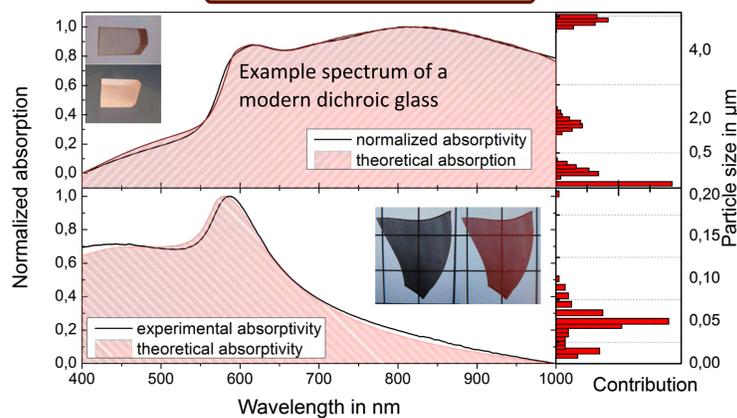


UV/Vis reflectance spectroscopy



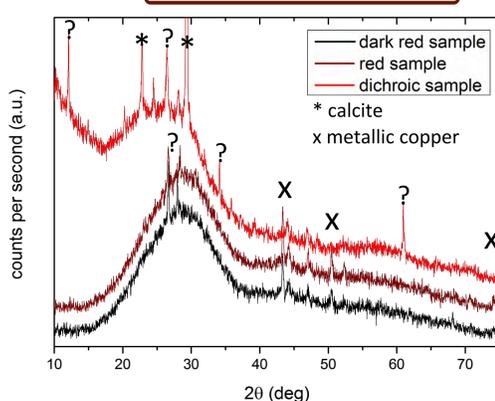
Transmission measurements on flashed glass from Wieda, Harz / Germany (17th ct. CE) were compared with Mie-scattering spectra simulated by MiePlot 4.5 [4]. The particle size distribution was estimated from the simulated values.

Simulated UV/Vis spectra



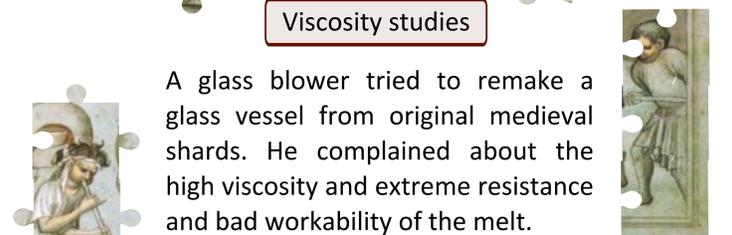
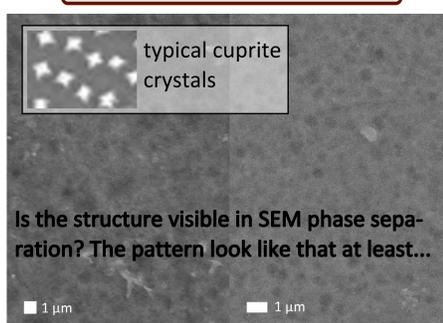
Can we confirm the particle size distribution?

X-ray powder diffraction



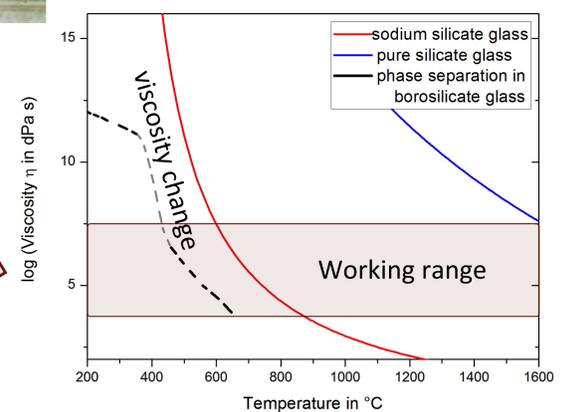
Opaque red glass does contain metallic copper particles. In case of the flashed glass the metallic copper was below the limit of detection. Calcite may have been formed as a corrosion product. Not all patterns could be explained yet.

Example SEM measurement



A glass blower tried to remake a glass vessel from original medieval shards. He complained about the high viscosity and extreme resistance and bad workability of the melt.

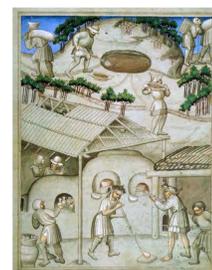
This reminded us to the viscosity-temperature-behaviour of phase separated glass: Phase separation leads to an immense viscosity increase [5].



The puzzle is not solved yet. Phase separation is a promising approach to explain the opacity of the red glass samples - like micro-crystals will droplets of phase separation scatter the light and induce opacity. The next step for us is to find the proof - maybe TEM and replica method will help. Replication of phase separated glass and UV/Vis analysis of sample slices will be investigated further.

Literature:

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- [4] MiePlot4.5: A software by Philip Laven (www.philiplaven.com/mieplot.htm). Last update: 10/11 2015
- [5] A. Flügel, Dissertation (Friedrich Schiller University Jena, 1999)



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