XAS Investigations of Ancient Egyptian Faiences

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Egyptian faience was produced over a period of approximately 5000 years, with the first examples dating to *ca* 4000 BC. Faience is a glazed, quartz-based material that was commonly used to make objects such as beads, pendants, rings, tiles, bowls, jars, gaming pieces and specialist funerary equipment [1]. The most common colours are light and dark blue, probably developed to imitate valuable stones, such as turquoise and lapis lazuli, but the colours red, yellow, white, purple and black also occur, albeit less frequently. Although faience is relatively common on archaeological sites dating from *ca* 1550 BC onwards, the chemical makeup and manufacturing techniques used to produce faience remain enigmatic.

We have investigated faiences of various blue and green colour tones using X-ray Absorption Spectroscopy (XAS) in order to assess the chemistry of the copper (Cu) colourant in the glazes. Experiments were conducted in fluorescence mode at bending magnet Beamline C at DORIS III. The Cu concentration in the glazes was fairly low (max. few %). In selected cases, both transmission and fluorescence scans were acquired showing consistent results, thus minimising self-absorption issues in fluorescence-XAS.

Results of the experiments are presented in Figure 1, showing a selection of five XAS scans of five faiences after background subtraction and normalisation to an edge jump of $\Delta\mu d = 1$. These five scans were selected as representatives from a series of *circa* 30 scans. This larger group of data was sorted according to statistical variations using Principal Components Analysis (PCA). Interestingly, this sorting (using principal component PC2) automatically resulted in the spectra being arranged according to the spectral feature at 9010 eV, just above the white line. Linear combination fitting
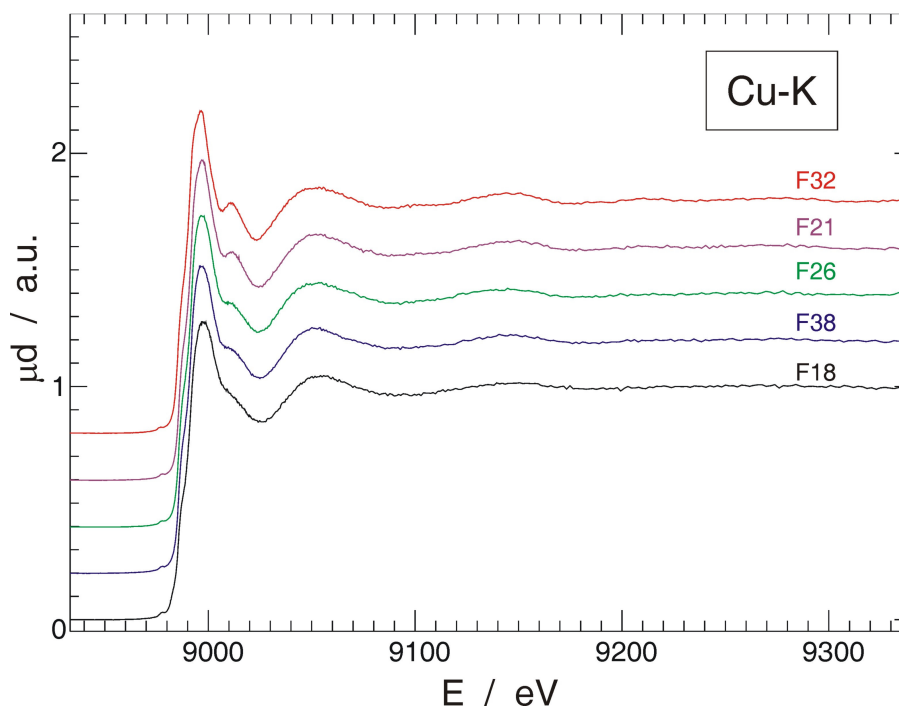

Figure 1: Selected XAS scans of five Egyptian faiences. For presentation purposes, the scans are plotted with a vertical offset of $\delta(\mu d) = 0.2$.

using the end-members of the series, samples F32 and F18, then indicated that the faiences in the series can fairly well be described as mixtures of these end-members. The results are shown in Table 1, indicating that throughout the series the relative concentration of spectroscopic components in the data shifts monotonously from 100% F32 to 100% F18. It is interesting that this behaviour in the series was correctly extracted by PCA without any prior knowledge of any order principles within the data set. This result also means that analysing the series' end-members, that is, spectra of F32 and F18, will already yield information on the chemistry and/or structure of the remaining spectra.

sample	c[F32] / %	c[F18] / %	R-value
F32	100	—	
F21	85	15	1.69
F26	46	54	1.16
F38	40	60	0.90
F18	—	100	

Table 1: Linear combination fit results of the faience spectra presented in
Figure 1 using the end-members of the series as input spectra for the fit.

For such further analysis, a set of reference spectra from copper containing minerals known to have been available in ancient Egypt was used. These minerals include turquoise, azurite, chrysocolla, dioptase, shattuckite, plancheite, and brochnatite. Linear combination fitting combined with PCA and target transformation showed that the data could not be described fully using either two, three, or four of the reference spectra available (fits with more input spectra were not attempted due the risk of the result being arbitrary, albeit mathematically viable). However, the fitting procedures indicated that in the case of F32, plancheite ($Cu_8Si_8O_{22}(OH)_4 \cdot (H2O)$; *ca* 70-80%) and either chrysocolla (($(Cu,Al)_2H_2Si_2O_5(OH)_4 \cdot n(H_2O)$)) or $CuCl_2$ were involved. Given the blue-green-turquoise nature of the faience beads, these results are sensible. For F18, the fits suggested linarite ($PbCuSO_4(OH)_2$) to be one of the key components mixed with one of a variety of potential other components, including Cu-hydroxide, azurite, dioptase or Cu-carbonate. This result indicates that in F18 Cu may be present in a structure that is similar to linarite, that is, a structure with oxygen in the first coordination shell and a heavy metal in a higher shell. Further structural work (e.g. powder diffraction and EXAFS) will be required to elucidate the precise nature of the faiences.

The results demonstrate that it is likely that the copper minerals used as colorants in the faience industry were by-products of the mining of minerals for use in smelting metallic copper. At known mining areas such as the Sinai, Egypt and Wadi Faynan, Jordan malachite ($Cu_2CO_3(OH)_2$) was the primary target of copper smelters. Plancheite, chrysocolla and azurite are known to co-exist with malachite at these mines and it is suggested that they may have been collected during the process of beneficiating the malachite ore by removal of extraneous surrounding minerals and gangue. Egyptian hieroglyphic texts at mining sites go some way to supporting this hypothesis, and based on these results, we can suggest that a hitherto untranslatable Egyptian word, *mafek*, might be now understood as any group of blue/green minerals for use in the pigments and vitreous materials industries.

References

[1] M.S. Tite & A.J. Shortland, 2008, *Production Technology of Faience and Related Early Vitreous Materials*. Oxbow Books: Oxford.