

Creating Egyptian Blue Pigment in the Laboratory: Practical Considerations and Insights into the Cuprorivaite-forming Reaction.

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Egyptian blue (EB) pigment was first identified as a silicate of copper and calcium in the 19th century. In 1938 the naturally occurring mineral cuprorivaite $\text{CaCuSi}_4\text{O}_{10}$, was discovered in the vicinity of Mount Vesuvius by Minguzzi (1938), and approximately 20 years later it was demonstrated that this was the phase responsible for the blue colour of EB. Subsequently, the terms *cuprorivaite* and *Egyptian blue* have commonly become interchangeable in usage. As observed on objects, EB invariably contains significant amounts of quartz (SiO_2 , see **Figure 1**) so it is suggested here that the term Egyptian blue be reserved for this material. The blue component of this pigment is the artificially-produced analogue of cuprorivaite (but note that, strictly, mineral names should not be used for artificially manufactured phases).

EB pigment available commercially appears to be pure cuprorivaite (**Figure 2**). This was considered too 'pure' in colour and, when mixed with appropriate binders, proved to be rather difficult to work with. Accordingly, a number of experiments were undertaken in order to produce a usable quantity of more workable and realistic-looking EB. In total, 14 experiments were conducted of which 9 produced significant amounts of EB, a total of 107 g in total. Experimental design was informed by a study of the available literature and by the results of a series of experiments conducted some years ago (Yiannopoulos, 2006). Though not the primary purpose, some insight was also gained into the nature of the cuprorivaite-forming reaction (CFR). The reader is referred to recent reviews by Kakoulli (2009) and Warner (2011) for a more comprehensive treatment of the subject.

Powder X-ray diffraction (XRD) was used to determine the phase composition of all starting materials, intermediate and final products. The presence (or otherwise!) of cuprorivaite was also examined using visible – infrared luminescence (VIL) imaging, as described by Verri (2008). See **Figure 3**. Quantities of starting materials were determined by calculation from stoichiometry, allowing for a *c.* 25% excess of quartz. Successful runs (*i.e.* those in which the final product was essentially cuprorivaite and quartz) had a molecular $\text{CaO}:\text{CuO}$ ratio close to 1.0. The most consistent results were obtained using a natural limestone (for CaO) and either a powdered bronze (IR350) or powdered copper metal (SP240) for Cu. The powdered metals are manufactured for use in glass fibre and resin castings and can be obtained from specialist suppliers (*e.g.* MB Fibreglass, www.mbfiberglass.co.uk) at modest cost. Finely sieved quartz sand was used in all runs as the source of SiO_2 .

Two other factors have been discussed, sometimes at length, in the literature (*e.g.* Warner, 2011). First, the nature of any flux used in the process. 'Flux' (generally an alkali salt) is necessary both to possibly lower the temperature at which the CFR takes place and to enhance rates of reaction. These are achieved probably by the formation of an intermediary glass, presumably of a Cu-rich Na-Ca-Si composition. In this work the simplest possible flux, laboratory grade Na_2CO_3 , was used. The amount of Na_2CO_3 was kept to 5 – 10% of the total reaction mass, a quantity that produces an amount Na_2O that can be incorporated into the cuprorivaite structure (Tite et al., 1984). Glass content cannot be determined by XRD. Since the phase composition of the final frit as determined (all be it inexactly) by XRD approached that

predicted by stoichiometry (**Figure 4**) it is assumed that the quantity of glass in the final product, if present at all, is at a minimum. The second factor is the nature of the vessel (crucible) in which the reaction takes place. This study found 'tall form' graphite crucibles were unsuitable, presumably because they did not allow liberated CO_2 to disperse away from the reactants. Tin-glazed porcelain crucibles of the type proved satisfactory, but evaporating dishes were of the most utility. The only down-side of using these crucibles was that sometimes the frit was difficult to remove without breaking the crucible but this seemed to be less of a problem with the evaporating dishes. Small amount of glaze sometimes came away with the frit but these fragments are readily identified and are easily removed.

The *exact* colour of the final product is possibly related to the initial proportions and nature of the starting materials but no clear relationship has yet become apparent. However, it is clear that grinding (grain size reduction) is an important factor, the colour of EB generally being intensified by grinding. These effects on final colour are currently under investigation.



Figure 1. A fragment of kiln lining with balls of EB adhering to its inner surface. XRD analysis (below) of a small portion of one ball indicates that the EB consists of cuprorivaite and quartz, with possibly some wollastonite and lime.

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CONCLUSIONS:

1. The CFR requires oxidising conditions. At the very least, CO₂ evolved during the process must be allowed to disperse.
2. The grainsize of the reactants, both initially and during the progress of an experiment, must be kept as fine as possible. At least three stages of manual grinding are recommended.
3. The CFR proceeds over a narrow range of temperatures, the lower limit being set effectively by the devolatilisation of calcite (c. 800 - 850° C). The upper temperature was not investigated here but is reported in the literature as c. 1000° C.
4. If quantities of flux are kept to a minimum (as here) the heating needs to be prolonged. The most successful experiments reported here were conducted at c. 860° C for in excess of 100 hours.
5. The most consistent results were produced using powdered bronze or powdered metallic copper as the source of copper.

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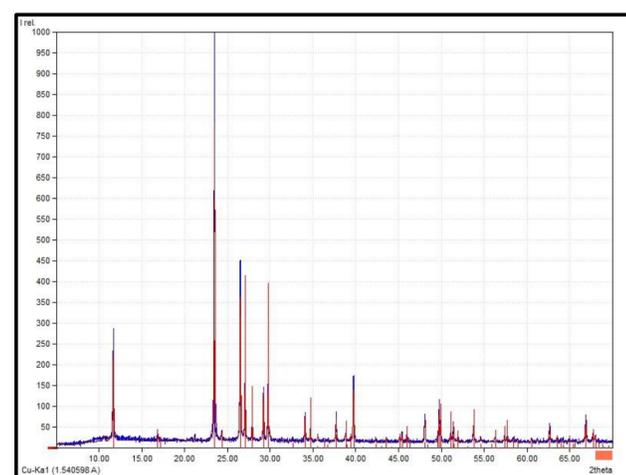


Figure 2 (above). XRD analysis of a commercial EB pigment. The material is essentially pure cuprorivaite.

Figure 3 (below). A selection of final frits imaged in normal light (upper panel) and by VIL (lower panel). Cuprorivaite is bright ('white') in the VIL images. Not all the frits contain cuprorivaite!

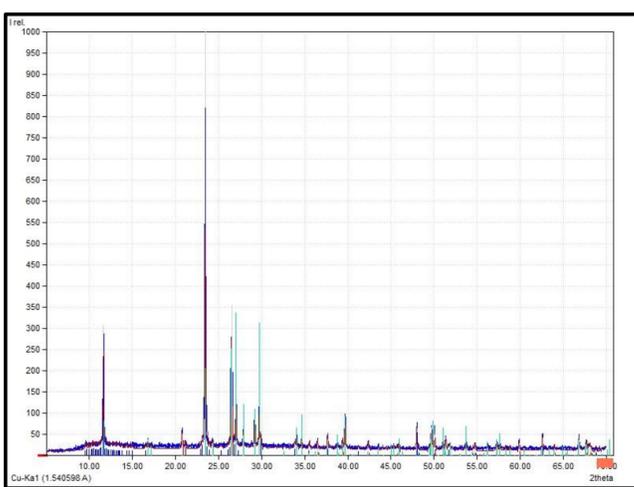


Figure 4 (left). XRD analysis of the final frit for sample IR350. Cuprorivaite and quartz are the only significant phases, tenorite (CuO) and cassiterite (SnO₂) present in trace amounts. See table below:

(wt. %)	calculated	XRD estimate
Cuprorivaite	84.4	75.1
Quartz	13.0	23.0
Tenorite (CuO)	Trace	1.5
Cassiterite (SnO ₂)	2.6	0.4

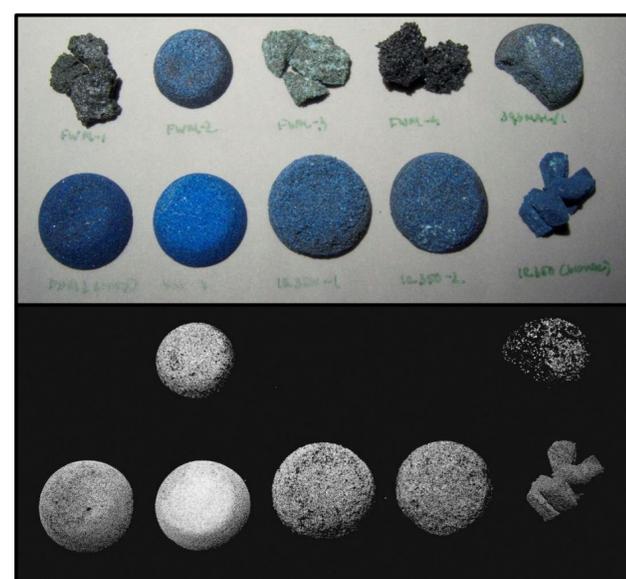
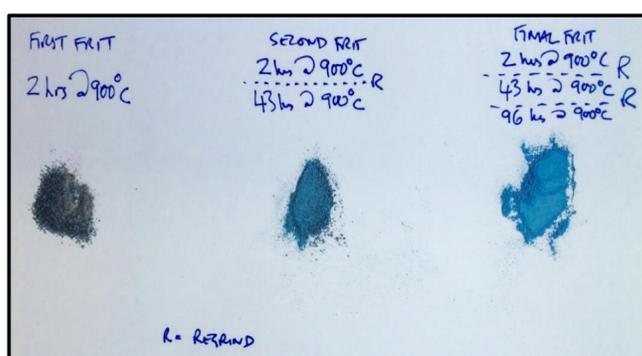


Figure 5 (below and below right). Progress of the CFR as reflected in (a) the appearance of the roughly-ground reaction products, below, and (b) by XRD, which shows clearly the increase on cuprorivaite as heating is prolonged. Note that glass cannot be detected by XRD.



Emmett panel 2/2

