Cambridge Archaeology Field Group

What makes a pot surface red or black in colour or with a different colour in the core.

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What makes a pot surface red or black in colour or with a different colour in the core of the section?

When out field walking, the pottery we recover can be of many different sorts and dates but also of different colours. Some examples are shown below (top – black burnished ware, bottom – Hadham sandy ware). One question that often arises is : what makes the pot surface go red or black?

Figure 1. Examples of different pottery surface colours. (Author's photograph)

Why do some pots have a core colour different to the surface colour, as shown in Figure 2, where the Much Hadham core is grey/black and the surface layer is red/orange.

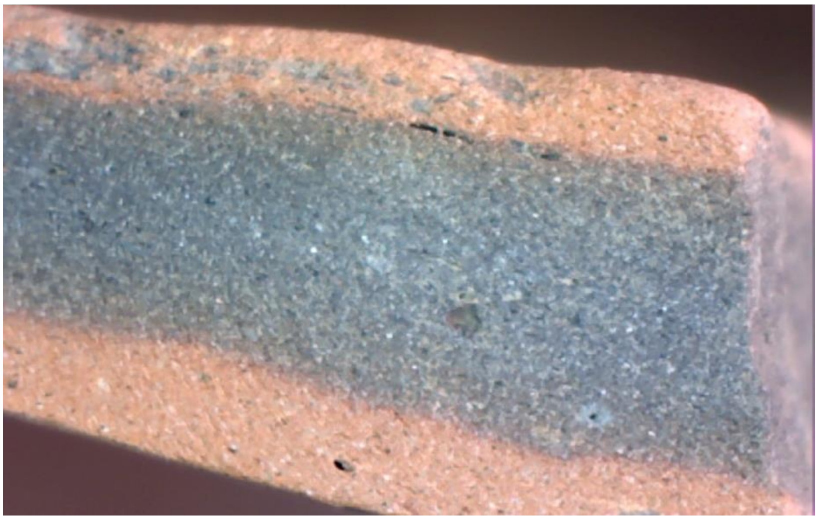

Figure 2. Cross-section of the Much Hadham red sandy ware (Author's photograph)

Contrast this with the cross-section view of a piece of Samian pottery, where the colour is uniform across the section.

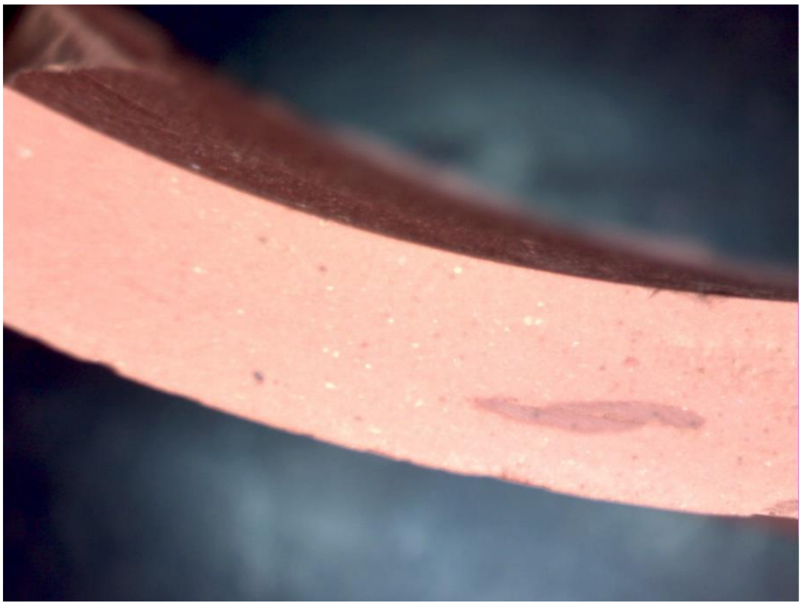

Figure 3. Cross-section of a Samian ware pot (Author's photograph)

The answer is – clay chemistry and kilns. There are a number of variables involved but the two most important are the clay and how it is fired. Clay factors included the size, quantity and distribution of impurities within the raw clay body. The impurities with the most impact are largely the presence of iron and carbonaceous material. The kiln firing conditions with the most impact are the firing time and temperature profile of the kiln and the atmosphere within the kiln in the latter stages of the firing.

Clays

Clays can be defined in a number of ways but generally by:

- The way they were deposited
- The type of impurities contained in them
- Their behaviour when heated in a kiln

1. Primary or residual clays are usually found on the site of their parent rock and only those minerals present in the parent are found as impurities. For example granite rocks may result in felspar, quartz or mica as impurities. The china clay deposits of St Austell in Cornwall are one such clay.
2. Secondary clays are those deposited away from their parent body by the action of agencies such as river water, glaciation, deposits in estuaries or lakes and occasionally as airborne deposits. During their formation they pick up impurities such

as lime, magnesia, alkalis, organic material and iron oxides. It is these impurities which have an impact on the colour of fired clay. They also contain smaller particles (typically less than 2 micrometres in diameter) and are more plastic as a result.

Main types of Clay

1. **Kaolin (China Clay)**: Composed predominantly of kaolinite ($Al_2Si_2O_5(OH)_4$). Kaolin is noted for its purity and high melting point. It has a low iron content, making it a white colour, and it is ideal for producing porcelain and fine china.

2. **Ball Clay**: Contains high levels of kaolinite along with other minerals such as quartz (SiO_2) and mica. It is highly plastic and workable so that it is often used to blend with other clays to enhance their plasticity and workability.

3. **Stoneware Clay**: Typically contains a mix of kaolinite, illite, and other minerals that provide durability and strength. It has intermediate plasticity and uses a higher firing temperature making it suitable for functional types of pottery like kitchen wares.

4. **Earthenware Clay**: Earthenware is more porous and less durable than stoneware or porcelain because it is fired at lower temperatures (typically between 1000°C and 1150°C). It is often used for decorative pieces and terracotta products.

Methods of firing pottery

A variety of firing techniques have been used over the centuries but the main types are listed below.

1. **Bonfire or pit firings**. Used since prehistoric times but continue in some parts of the world today. This was originally a domestic activity, probably using the cooking hearth to carry out the firing. This became more of a communal occupation with the bonfire firing. Here the pottery was stacked together and the fuel, normally wood but also fuels like sawdust or dried dung, is heaped over the pottery and set fire. Temperature rises rapidly to its maximum and then falls away more slowly. There is no control of the conditions with respect to the atmosphere surrounding the pottery. Examples are shown in Figures 4 and 5 below.

Figure 4. A simple bonfire firing of pottery at a domestic level.

Figure 5. A communal firing of pottery in sub -Saharan Africa today (Photograph by Marco Belluci, https://www.flickr.com/photos/marcobellucci/3452949446/sizes/l/)

2. This method of firing pottery was superseded in later periods by **Updraught kilns**, shown in Figure 6, which gave much better control of the conditions during a firing. An updraught kiln is any structure where the fire is set below the stacked pottery

which is enclosed by a dome made of a variety of materials. A vent or chimney in the roof allows the smoke and combustion products to escape. Updraught kilns give more uniform temperatures and retain heat better than simple bonfire kilns. Temperatures up to 900°C can be attained in this type of kiln, when fired with wood. In these kilns, there is no control over the air flow rate, while the fuel burning rate is controlled by adjustments to the fuel feed rate in the stoke hole.

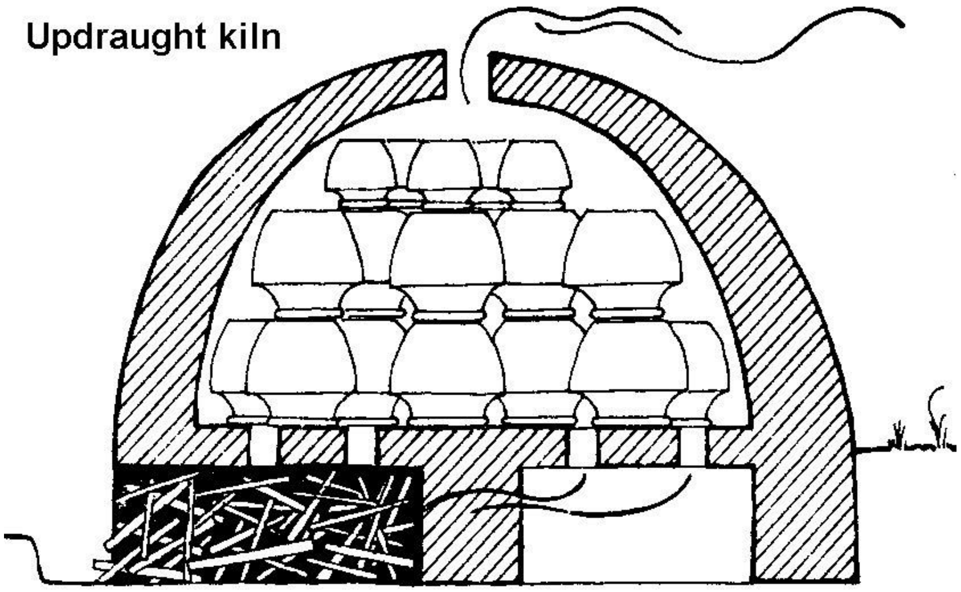

Figure 6. Example of an updraught kiln. (Taken from Hodge, 1976)

3. A modification is the **Downdraught kiln**, seen in Figure 7 below.

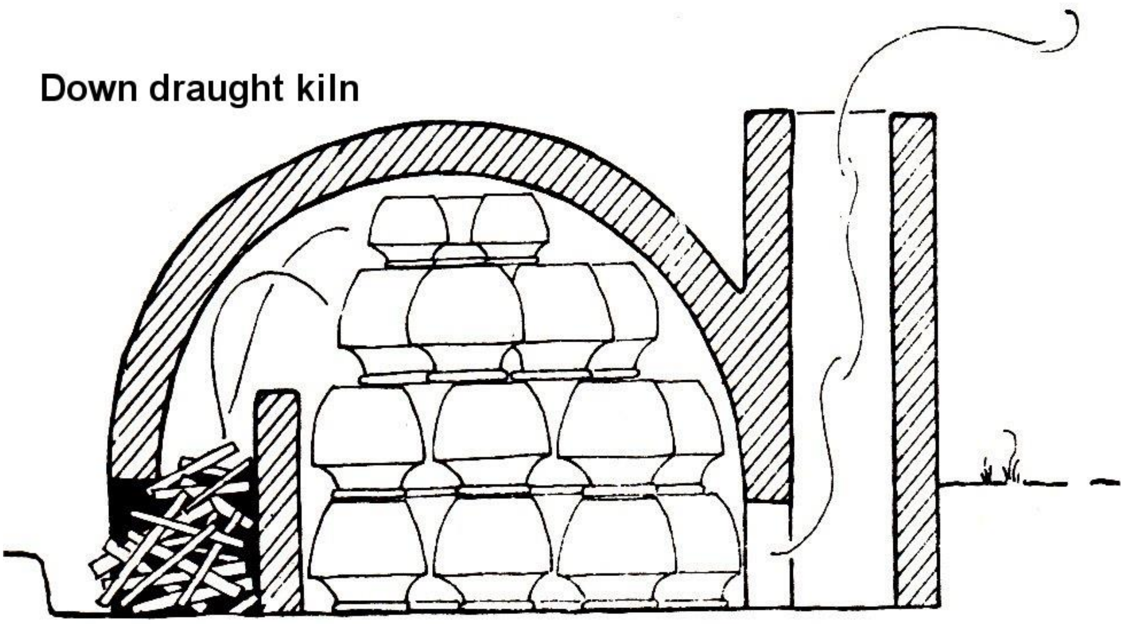

Figure 7. Example of a down draught kiln. (Taken from Hodge, 1976)

Here the chimney is connected to the bottom of the kiln and the hot gases produced in the stoke hole are drawn through the kiln in such a way that initially the hot gases flow upwards and then flow downward due to the pull from the chimney. The temperatures achieved range from 1500-1600°C and there is better uniformity and control over firing than with an updraught kiln.

Modern kilns are variations on these types but using coal, gas, oil or electrical heating. Bottle kilns, of the type shown in Figure 8, were mostly built for pottery production in the later 18th and the 19th centuries. Although very inefficient (each firing took some 14 tons of coal but some 70% of the energy of the fuel was wasted), bottle kilns were constructed until the mid-twentieth century, after which they were replaced by other types of kiln, as the industry ceased to be coal-fired. The Clean Air Act of 1956 marked the end of their use in the United Kingdom. The example shown is from Longton, part of the Stoke on Trent industry.

Figure 8. Bottle kiln design

(Photograph from Chris Allen, CC BY-SA 2.0, https://commons.wikimedia.org/w/index.php?curid=13212922)

Forming and firing pottery

After the pottery has been formed by the potter it requires a period of drying. As clay dries, water evaporates causing the clay particles to draw closer together, resulting in shrinkage that can lead to cracking if not managed properly. Drying prevents steam damaging the pot during the firing and changes the clay to a stronger body called the green-hard or leather-hard state. It is in this condition that activities like burnishing and adding handles and decoration take place. The pot is then ready for firing.

After the pottery has been arranged in the kiln a small fire is lit to slowly raise the temperature and drive the remaining water of plasticity out. This may take some time.

The fire is then increased in size and the temperature allowed to rise slowly. This causes a series of chemical and physical transformations to take place in the clay. The key reactions during firing include:

1. ***Dehydration**: Around 100-200°C, the physically bound water held in pores evaporates.*
2. ***Dehydroxylation of chemically bound OH**: At approximately 450-600°C, hydroxyl groups (-OH) in the clay minerals are expelled, for instance converting kaolinite to metakaolin ($Al_2Si_2O_7$).*
3. ***Quartz Inversion**: Around 573°C, quartz undergoes a reversible transformation from the alpha (low) to beta (high) phase, which can cause expansion and contraction.*
4. ***Vitrification**: As the temperature increases to 800-1300°C (depending on the clay type), the silica and alumina components start to melt and form a glassy matrix. This process, known as vitrification, is crucial for developing the strength, density, and impermeability of the pottery.*

The Colouring Process

The colour of fired clay is largely influenced by the iron compounds in it and by their state of oxidation together with the amount of carbonaceous material in the raw clay. The simple version is that, with little iron present in the clay, pottery is typically off-white or buff (though orange-yellow, grey or brown cores are sometimes seen). Conversely, clay rich in iron compounds becomes highly coloured when fired with normal levels of oxygen, resulting in a red, tan, or brown colouration. However, if the kiln was sealed towards the end of firing, a reducing atmosphere is formed (where oxygen is absent or much reduced) and the pottery may become blue grey to almost black in colour. The complete story is, however, more complex.

In simple bonfire firings there is little control over the conditions, especially the amount of oxygen present. Pots may be covered in ash or unburnt fuel may cover parts of a pot so the result is a surface partly oxidised to a red colour and partly reduced to a black colour, resulting in a blotchy appearance. Vessels may have a dark core which is a sign of a brief firing where insufficient time is allowed to burn out all the organic material in the body – this is not due to a reducing atmosphere being present. Also, magnetite (ferrous-ferric) iron compounds remain black at low temperatures. The thicker the vessel wall, or the less porous the fabric, the more likely that carbon will not be fully burnt out. However, heating for longer at the same temperature may eventually result in the disappearance of the core.

As mentioned before, the use of kiln structures gave potters more control over the firing conditions and hence more control over the final surface colour of their pots.

1. In a kiln burning dry fuel and with a good through draught there will be excess oxygen and the conditions are said to be oxidising. If the temperatures are high enough then all the carbon in the fuel and in the pottery itself will be converted to CO_2 and lost as gas. The more porous the pottery fabric the easier this occurs.

   $$C \text{ (solid)} + O_2 \text{ (gas)} = CO_2 \text{ (gas)}$$

2. At the same time all the iron compounds will be converted to red ferric oxide, (Fe_2O_3) hence the red colouration of pottery made in this fashion (as seen in the lower example in Figure 1).
3. In a kiln burning damp fuel and/or with a restricted draught, there will be much reduced oxygen levels and the conditions are said to be reducing. Here the gases will typically have high carbon monoxide concentrations – this is oxygen hungry and will take it from any available source such as the iron oxides in the clay. This reduces the iron to lower oxides which are dark grey or black in colour, hence the black/grey colouration of the pottery fired under these conditions (as seen in the upper example in Figure 1).

   $$3\,Fe_2O_3 + CO = 2\,Fe_30_4 + CO_2$$

   red oxide black magnetite

4. Under reducing conditions, not all the fuel and the carbonaceous material in the clay will be burnt and a smoky atmosphere containing lots of free carbon will result. This free carbon (also called soot), will be deposited on the pottery surfaces and will fill the pores of the fabric – this is called smoking or smudging.

This intensifies the dark colouration and the same effect may be seen on pottery used for cooking in fires.

5. There are, of course, intermediate states where a kiln fired under reducing conditions is opened while cooling and the oxygen in the air will then oxidise the surface layers of the pottery but not the internal fabric. This results in pottery like that shown in Figure 2.

The use of a coloured slip

The colour of fired clay can be altered by the firing process but another technique is the use of a coloured surface slip. A classic example here in Cambridgeshire is the colour coated Nene Valley pottery we find so regularly. The Nene Valley fabric fires to a creamy-white colour in normal circumstances but the application of slip results in the brown to black colouration we often see.

Figure 9 shows a beaker found at Itter Crescent, Peterborough where the brown slip has worn through to expose the underlying white fabric of the vessel.

(https://peterborougharchaeology.org/fane-road-roman-villa/roman-pottery-types/

Figure 9. Nene valley beaker with orange/brown slip

A slip is a liquid suspension of very fine clay particles in water that is applied to the leather hard pot, usually by dipping, pouring or painting. The clay used is high in iron compounds which results in the same colourations as described earlier, i.e firing red/brown to black depending on the kiln conditions. Technically a slip is not the same as a glaze, although it may serve some of the same functions, i.e. to reduce porosity. Another slip we see is that which gives Roman Samian pottery its deep red, glossy finish. Samian pottery uses a clay fabric high in iron content and is typically rich in calcium so that it fires deep red in oxidising conditions. The slip contains a higher proportion of iron, potassium and sodium, which allows it to melt onto the body of the vessel to give the glossy finish.

Conclusions

The advent of the enclosed kiln gave potters much better control of conditions such as the temperature and oxidising/reducing atmosphere within the kiln. With this they were able to control the surface colour/appearance of the pottery, presumably to satisfy the fashion of the day.

References

Useful reference books for more information are:

Prehistoric pottery for the archaeologist, Gibson & Woods, Leicester university Press, 2nd edition 1997.

Artifacts – An introduction to early materials and technology, Hodges, Bristol Classical Press; New edition (26 Jan. 1995).

Pottery Analysis – a source book, Rice, University of Chicago Press, 1987.

Roman pottery in Britain, Tyers, Routledge, 1996.

Shire Archaeology publish a series of books covering pottery from various periods.

The National Roman Fabric Reference Collection – A handbook by Tomber and Dore can be downloaded or viewed from the Study Group for Roman Pottery website.

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