

My aim in this brief article is to record a snapshot of evolving perspectives on several surface color-development phenomena that occur when we wood fire unglazed clay. In my presentation at the NCECA 2022 conference I will showcase empirical evidence in the form of microscope images and spectroscopic data acquired directly from wood-fired pots; here I will highlight a selection of insights (and references) from contemporary materials science that seem most relevant for interpreting such images and data.

Clay comprises weathered minerals of the Earth's crust. As such, its primary elemental constituents<sup>1</sup> are oxygen, silicon, aluminum, iron, calcium, sodium, magnesium, and potassium. Before firing, these elements are incorporated within specific mineral compounds and aggregates that constitute our plastic clay bodies<sup>2</sup>. When we fire bare clay to stoneware temperatures in a wood-burning kiln, the surfaces of our pots undergo a complex series of transformations that can produce a remarkable range of colors and textures on the finished work. These colors and textures evidently result from localized physical processes involving just the material constituents of clay, fly ash, and the complex kiln atmosphere produced during firing and cooling. As potters we would like to understand these processes in ways that help us achieve desired results and point us towards new firing experiments.

The atmosphere in a wood-burning kiln at high heat is incredibly complex, containing not only combustible gases, air, and fly ash, but also flux gases such as sodium and potassium. Within the broad portfolio of wood-fire surface effects, it seems reasonable to start with colorations that form on surface patches that have been fluxed and perhaps otherwise chemically altered (e.g., carbonized) by kiln gases, but have not been covered by a significant amount of deposited ash<sup>3</sup>. This subset of effects would include for example what most people would call flashing, as well as the development of reduction-cool reds, both of which are currently believed to be caused mainly by redistribution/reconfiguration of iron.

Iron can be found in distinct material contexts (phases) within unfired clay bodies. Iron atoms can be incorporated as impurities within clay minerals themselves – for example, kaolinite has the ideal composition  $\text{Al}_2\text{Si}_2\text{O}_3(\text{OH})_4$  but ferric iron ( $\text{Fe}^{3+}$ ) can take the place of aluminum atoms within the kaolinite crystal structure<sup>4</sup>. Iron atoms can similarly substitute or intercalate within the nominal crystal structures of more complex clay minerals such as smectites and illites<sup>5</sup> and can be incorporated within the crystal structures of feldspars<sup>6</sup>. Iron can of course also enter unfired clay bodies in the form of particulate iron oxides/hydroxides (such as hematite, magnetite, goethite, ilmenite, etc.) that are either present in the as-mined clays/feldspars or intentionally added.

What happens to all these iron atoms when clay bodies are fired – and cooled – under various temperature and reduction/oxidation (redox) schedules? And how does the complex atmosphere of a wood-burning kiln complicate the story? If we can work out comprehensive answers to these questions

we will understand a major part of wood-fire color formation, but these are expansive questions and contemporary materials science so far enables us only to formulate narrow hypotheses and suggest explanations of limited scope. By taking our first small steps along this road we can begin crafting a framework for thinking more broadly about wood-fire color formation, which in turn can help us focus on some sensible next steps.

Numerous scientific studies have sought to track the fate of iron impurities when kaolinitic clays – without any admixed feldspar – are transformed by heat. Djemai and co-workers report<sup>7</sup> that isolated iron atoms that start as substitutions in the kaolinite crystal structure are exsolved in the temperature range of 900-950 °C (approximately Cone 010-08 under their firing conditions) and become available for incorporation in other mineral structures. When their samples are heated *in oxidation* above 1200 °C (approximately Cone 5), Djemai *et al.* find that most available iron atoms are incorporated into mullite crystals that begin to form at these high temperatures. In a similar study, Ceylantekin and Başar found<sup>8</sup> that essentially all the iron from a 4 wt% addition of fine hematite particles to kaolin can be absorbed into mullite formation with a 3-hour soak at 1300 °C. With increasing iron impurity content, macroscopic mullite crystals are known to change from clear to yellow, and eventually brown; extremely small (sub-micron) iron-containing mullite crystals may not impart significant coloration to the ceramic matrix at all<sup>9</sup>. If sequestered within mullite in this fashion, iron is not available to participate in the formation of reddish mineral pigments as the kiln cools (see below).

Although the materials we use in wood-fire ceramics tend to be more complex than straight kaolin, the results of these studies suggest that flashing and other iron reds may be promoted by avoiding prolonged oxidation while the kiln is above mid-fire temperatures. Reduced iron has a larger ionic radius (is a larger atom) and cannot fit within the mullite crystal structure the way oxidized iron can<sup>10</sup>, hence, keeping the iron atoms reduced at high temperature suppresses the tendency for them to become trapped in mullite. At the same time, these findings help us understand how some light stoneware clays become pink or brick-colored when bisque fired (iron exsolved from the decomposition of metakaolin forms hematite) yet buff when high-fired in oxidation (iron is sequestered in mullite); similar factors may explain why most porcelains are whiter in oxidation than in reduction.

Kusano, Fukuhara and co-workers have performed extensive studies<sup>11</sup> on the red-coloration effect known as *hidasuki* within the Bizen tradition of Japanese wood-fired stoneware pottery. They show that the red “cord marks” of *hidasuki* are associated with localized fluxing of the ceramic surface by potassium released from combustion of rice straw that is wrapped around pots (originally as a form of wadding). Notably, this surface effect can be produced on Bizen clay (an iron-bearing stoneware) even in

an electric kiln oxidation firing (to 1250 °C) with an appropriate cooling schedule. The red color comes from clusters of small hematite crystals that grow around the edges of larger corundum ( $\text{Al}_2\text{O}_3$ ) crystals and increases in intensity with slower and more oxidized cooling conditions. For the same firing up to 1250 °C, the final surfaces are greenish-ochre if quench-cooled, reddish-orange if cooled in air at 10 °C/min or dark (brownish) red if cooled in air at 1 °C/min. Development of red color is strongly suppressed even at the slow cooling rate of 1 °C/min if the oxygen content of the kiln is reduced.

I have observed very similar hematite-corundum crystal clusters to those studied by Kusano *et al.*, in the surface layer of a light stoneware clay fired in a kazegama<sup>12</sup> (gas kiln with blown ash introduced at Cone 9-10), leading me to believe that this type of corundum-nucleated formation of hematite crystal clusters may be responsible for a wide range of red “flashing” effects – flux gases in a wood or other atmospheric kiln can substitute for potassium released by burning rice straw in the *hidasuki* scenario, and I think it is fair to say that many coloration effects we categorize as flashing occur in slightly-glossy patches that have not been covered by fly ash. In the microscope images I have collected of the hematite-corundum clusters (see image accompanying this article), there is a notable diffuse yellow background that could be the result of iron incorporation within mullite crystals as discussed above.

A quite distinct red surface coloration can be produced by delayed reoxidation of iron-bearing stoneware clays. These so-called “reduction-cool reds” are characterized by a velvety visual texture and generally appear against a grey-black background. In joint work with Dan Murphy, John Neely, and their students at Utah State University, we have used scanning electron microscopy, energy-dispersive spectroscopy, and micro-Raman spectroscopy to analyze the nature of these red surfaces. Unlike flashing reds, in which hematite crystal pigments are buried within a glassy matrix, exposed iron oxide crystals grow up and out of the ceramic surface in patches of reduction-cool red. While there is still much to be studied, it seems quite likely that reduction-cool reds are formed by a microphysical process discovered by Reid Cooper and his laboratory. Cooper and co-workers performed experiments<sup>13</sup> in which reduced iron-bearing alkaline-aluminosilicate glass samples were melted at high temperature and then cooled, with re-oxidation occurring either above or below their glass transition temperature. In samples that were re-oxidized at higher temperatures, oxygen would diffuse into the surfaces and oxidize iron atoms in place (still buried within the glass), but when re-oxidation was delayed to lower temperatures the iron atoms would be pulled up to the surface (the air-glass interface) and accumulate there as a thick layer of iron oxide crystals.

In our studies of wood-fired ceramic surfaces we see direct evidence for this remarkable phenomenon in the fact that reduction-cool red patches generally have far higher iron content than the

bulk clay body and can confirm using Raman spectroscopy that the mineral composition of these patches is dominated by iron oxides. Morphologically we see that reduction-cool red patches are conglomerations of microcrystals that look like they are growing up and out of the surface, while associated black surface regions are glassy (aluminosilicate in elemental composition) and smooth (in micro-texture). The structural details of some electron micrographs reinforce the interpretation of iron oxide crystals being “pulled up” out of the depths of the ceramic surface – for example, one often sees the beginnings of iron oxide crystal accumulation within cracks in the black aluminosilicate glass – and provide at least anecdotal evidence against an alternative hypothesis that reduction-cool reds are created by deposition of gaseous iron from the kiln atmosphere.

I find it intriguing how the above vignettes underscore similarities between ceramic wood firing and igneous (or perhaps pyrometamorphic) petrology. As previously mentioned, clay comprises weathered minerals of the Earth’s crust and firing pots to stoneware temperatures in a fluxy atmosphere creates a surface layer of aluminosilicate melt that is not so dissimilar from magma<sup>14</sup>. As the pots cool, crystals nucleate within this glassy/liquid skin; the temperature and redox schedule of the firing *and cooling* strongly influence what kinds of minerals form. Variations in the mineral assemblages (and the composition of the residual glass) thus produced determine in turn the final surface colors and textures of the pots at room temperature, much as is the case with lava cooling into rocks. As for next steps, my current thinking is that we should try to understand in detail some of the predominant mechanisms by which our wood-fired surfaces turn brown<sup>15</sup>.

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<sup>1</sup> [https://en.wikipedia.org/wiki/Abundance\\_of\\_elements\\_in\\_Earth%27s\\_crust](https://en.wikipedia.org/wiki/Abundance_of_elements_in_Earth%27s_crust)

<sup>2</sup> Of course, organic carbon- and sulfur-containing species are also present but generally burn out below bisque temperatures.

<sup>3</sup> It seems likely that the processes by which such effects are produced could be similar in wood firing and in soda firing.

<sup>4</sup> S. Petit, J. Madejova, A. Decarreau, and F. Martin, “Characterization of Octahedral Substitutions in Kaolinites Using Near Infrared Spectroscopy,” *Clays and Clay Minerals* **47**, 103 (1999).

<sup>5</sup> J. W. Stucki, “Chapter 11 – Properties and Behaviour of Iron in Clay Minerals,” *Developments in Clay Science* **5**, 559 (2013).

<sup>6</sup> A. M. Hofmeister and G. R. Rossman, “Determination of Fe<sup>3+</sup> and Fe<sup>2+</sup> concentrations in feldspar by optical absorption and EPR spectroscopy, *Physics and Chemistry of Minerals* **11**, 213 (1984).

<sup>7</sup> A. Djemai, E. Balan, G. Morin, G. Hernandez, J. C. Labbe, and J. P. Muller, “Behavior of Paramagnetic Iron during the Thermal Transformations of Kaolinite,” *Journal of the American Ceramic Society* **84**, 1017 (2001).

<sup>8</sup> R. Ceylantekin and R. Başar, “Solid solution limit of Fe<sub>2</sub>O<sub>3</sub> in mullite crystals, produced by kaolin from solid state reactions,” *Ceramics International* **44**, 7599 (2018).

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<sup>9</sup> A. Djemai, G. Calas, and J. P. Muller, "Role of Structural Fe(III) and Iron Oxide Nanophases in Mullite Coloration," *Journal of the American Ceramic Society* **84**, 1627 (2001).

<sup>10</sup> H. Schneider, "Solubility of TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and MgO in Mullite," *Ceramics International* **13**, 77 (1987).

<sup>11</sup> Y. Kusano, M. Fukuhara, J. Takada, A. Doi, Y. Ikeda, and M. Takano, "Science in the Art of the Master Bizen Potter," *Accounts of Chemical Research* **43**, 906 (2010).

<sup>12</sup> Steve Davis, <https://kazegama.com>

<sup>13</sup> D. R. Smith and R. F. Cooper, "Dynamic oxidation of a Fe<sup>2+</sup>-bearing calcium-magnesium-aluminosilicate glass: the effect of molecular structure on chemical diffusion and reaction morphology," *Journal of Non-Crystalline Solids* **278**, 145 (2000); G. B. Cook and R. F. Cooper, "Iron concentration and the physical processes of dynamic oxidation in an alkaline earth aluminosilicate glass," *American Mineralogist* **85**, 397 (2000).

<sup>14</sup> Iron oxide surface layers very similar to reduction-cool reds have even been found on basaltic lava flows: D. J. M. Burkhard and H. Müller-Sigmund, "Surface alteration of basalt due to cation-migration," *Bulletin of Volcanology* **69**, 319 (2007).

<sup>15</sup> One such mechanism has recently been described by Kusano, Fukuhara and co-workers: Y. Kusano, H. Nakata, Z. Peng, R. S. S. Maki, T. Ogawa, and M. Fukuhara, "Studying and Utilizing Traditional Technologies: Microstructure and Formation Mechanism of ε-Fe<sub>2</sub>O<sub>3</sub> on Traditional Japanese Bizen Stoneware," *ACS Applied Materials & Interfaces* **13**, 38491 (2021).