Iron Colourants in Athenian and Boeotian Pottery from Ancient Greece, c.500-100BCE, with Synchrotron XRD and XANES

Chia-Lin Hsu (許家琳)[1*], I-Jui Hsu (許益瑞)[2], Jyh-Fu Lee (李志甫)[3],
Hwo-Shuenn Sheu (許火順)[3], Jey-Jau Lee (李之釗)[3]
[1]History Department, Tunghai University, Taichung, Taiwan
[2]Department of Molecular Science and Engineering, National Taipei University of Technology, Taipei, Taiwan
[3]National Synchrotron Radiation Research Center, Hsinchu, Taiwan
hcl@thu.edu.tw

Abstract

Pottery with colours of red and black is one of the most famous products of ancient Greece, c. 500-100BCE. Past studies propose a theory that the colours are due to iron oxides, but experiments have not directly proved this. The problem lies in the fact that the colourants are often smaller than 1 μm and may be both crystals and amorphous. With SEM-EDS and synchrotron XANES, we rarely found heavy metals other than iron in the pottery, and it should be certain that the colours relate to iron. We have tried to identify iron's oxidation state as well as iron-containing crystals in the pottery, with synchrotron XRD and XANES. So far, the XANES data show that the samples of the Athenian type of the pottery are similar to each other in terms of iron contents. They all probably contain the same materials, although the amounts may vary. One sample's spectrum looks like the others' but shifts a little, which may result from the effect of some different materials in the pottery. The XRD data of the black colour of one sample show that iron oxides such as magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), wüstite (FeO) may exist, recalling the theory proposed by past studies. However, we have found that so many other crystals in the pottery may contain iron, such as chayesite ($K_4Mg_6Fe_4Si_{24}O_{60}$), the olivine group (Ca_2SiO_4-Mg_2SiO_4-Fe_2SiO_4), and the pyroxene group (XYZ_2O_6, $X=Na^+$, Ca^{2+}, Mn^{2+}, Fe^{2+}, Mg^{2+}, Li^+; $Y= Mn^{2+}$, Fe^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, Cr^{3+}, Ti^{4+}; $Z=Si^{4+}$, Al^{3+}). They often associate with silicate. The data indicate that the colour of the pottery not only relates to iron oxides, but also to many other iron-containing silicates. This may also indicate that the raw material of the black colour came from a natural environment where iron oxides and silicates co-existed, which may have not been rare in the Mediterranean region. Our samples include the Athenian and Boeotian types of the pottery, and the hues of these two types are not exactly the same. We are to explain why the two types look different in the light of the iron content.

Keywords – Ancient Greece, Athens, Boeotia, pottery, colour