Using X-ray diffraction to elucidate source materials and firing conditions of Pompeian ceramics

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Numerous archeometric and analytical studies have been made of the ceramic materials unearthed in and around Pompeii, all of which represent invaluable sources of archaeological data, shedding light on ancient Roman habits, culture, and technology. A large amount of pottery has been discovered, and recently Cavassa et al. (2014) discovered an outstanding and unique example of a Roman ceramic workshop (*Via dei Sepolcri*), including the equipment and raw materials, along with unfired, fired, and overfired shaped vessels used on the day in 79 AD just before the eruption (Grifa et al., 2013). These materials allow tracking both the source materials and firing process(es) used by the ancient artisans. Many sources have been proposed, including local marine, volcanic, and fluvial or lacustrine clays. Clarification of the source(s) of the clays would expand our understanding of trade routes and mechanisms of transport and trade. The clay raw materials and the unfired vessels unearthed in the *Via dei Sepolcri* workshop in Pompeii represent an important opportunity for such clarification, and the occurrence of fired and unfired specimens allows us to clarify the mineralogical transformations of clay and other minerals caused by firing. We are using a two-pronged approach to analyze these materials using X-ray diffraction (XRD) and trace element geochemical methods (e.g., rare earth element geochemistry). Data in Fig. 1 represent the mineralogy of the

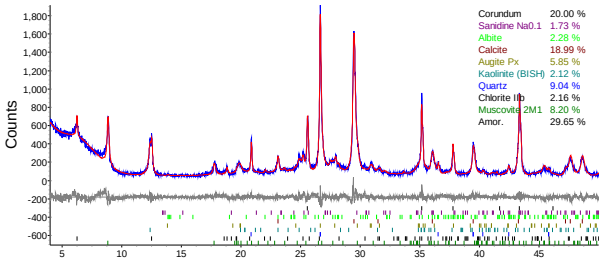

Figure 1. Rietveld fit to XRD data (CuKα) for unfired pottery material from *Via dei Sepolcri*, Pompeii, showing diffraction peaks from phyllosilicates (amorphous component represents unmodeled smectite; 20% corundum internal standard). Observed data: blue; calculated: red; background: gray.

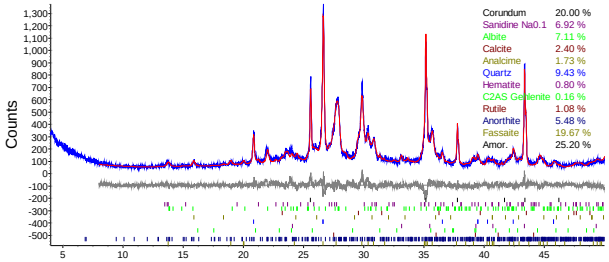

Figure 2. Rietveld fit to XRD data (CuKα) for a pottery sample that was obviously fired, showing the absence of peaks from phyllosilicates, the presence of high-T oxide and silicate products, and a large amorphous component. Conventions and corundum standard as in Fig. 1.

unfired material; the presence of chlorite, kaolinite, and an illitic material, all hydrous phyllosilicates, indicates that the material is unfired, and the presence of calcite ($CaCO_3$, primarily foraminifera, based on microscopic examination) is apparent. The thermal behavior of these individual minerals is well understood, and XRD analysis of partially, normally, and overfired materials sheds considerable light on firing temperatures and times used almost 2,000 years ago for pottery production. The data in Figure 1 contrast with those of Figure 2, showing a similar Rietveld fit using data for another sample from the same kiln; based on the absence of hydrous phyllosilicates and the presence of high-temperature products, this sample was obviously already fired. In general the fired and overfired ceramics contained a large amount of amorphous material, from 1/3 to almost 2/3 of the ceramic product, and most clay minerals and calcite have been destroyed, consistent with firing temperatures of 850-1000°C. Significantly, the Pompeiian ceramics do not contain detectable gehlenite ($Ca_2Al[AlSiO_7]$), a member of the melilite group that is common in similar products fired between 850° and 1000°C (i.e., the "gehlenite problem," Heimann, 2017). Heimann suggests that its absence results from the narrow and small grain size distribution in the raw materials of higher-quality ceramics, whereas coarse, low-fired wares of similar mineralogy contain significant gehlenite. The potential for some post-or syn-eruption alteration is suggested by scanning electron microscope evidence for zonation and/or reaction rims around pores and temper.

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