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*Hein - PYROCER - Investigation of pyrotechnical ceramics from the Workshop of Phidias in Olympia, Greece (User Report)*

## **PYROCER - Investigation of pyrotechnical ceramics from the Workshop of Phidias in Olympia, Greece**

*User Report – ARCHLAB Visit of Anno Hein at the Rathgen Forschungslabor*

*(Berlin, 9<sup>th</sup> – 20<sup>th</sup> July 2018)*

**Anno Hein**

Institute of Nanoscience and Nanotechnology, N.C.S.R. "Demokritos", PO Box 60037,15341  
Aghia Paraskevi, Attica, Greece – [a.hein@inn.demokritos.gr](mailto:a.hein@inn.demokritos.gr)

### **Introduction**

Scope of the present project is the investigation of pyrotechnical ceramics, which were excavated in the 'Workshop of Phidias' in Olympia (Greece), a bronze casting workshop in the vicinity of the sanctuary dated to the 5th century BC (Heilmeyer et al. 1987, Zimmer 1990, pp. 39-51), and in a contemporary workshop in the Athenian craftspeople quarter Kerameikos (Heilmeyer et al. 1987). Fragments of these pyrotechnical ceramics, including furnaces, crucibles, casting molds and tuyères, have been examined during the 1980s (Schneider and Zimmer 1984, Heilmeyer et al. 1987) and a part of this assemblage has been preserved in the 'Antikensammlung' Berlin. The present ARCHLAB visit was focused on a complementary examination of selected samples of this material, particularly of crucibles and casting moulds, using microscopic methods, such as optical microscopy (OM) and scanning electron microscopy (SEM) and mineralogical examination by Fourier-Transform infrared spectroscopy (FTIR). Among other results new findings concerning microstructure and micromorphology of the ceramics were expected, providing information about the fabrication of the ceramics as well as the actual metallurgical processes, which they were used for. This was of particular interest in view of our project investigating Protogeometric and Geometric bronze tripod cauldrons (funded by the German Research Foundation; coordinated by Dr. M. Kiderlen, Humboldt University). Within the framework of this project we have examined residues of Geometric casting ceramics, sampled from casted tripod fragments, found at the sanctuaries in Olympia and Kalapodi (Kiderlen et al. 2017). Apart from these comparatively small residues there was no further evidence for casting workshops of the Geometric Period at the two sanctuaries. Nevertheless, the hitherto results proved local production of bronze tripod cauldrons, based mainly on the used raw materials, and provided basic information about casting technology and fabrication technology of

casting ceramics during this period. In the case of Kalapodi it was furthermore possible to sample crucibles, molds and tuyères from a Classic bronze casting workshop for a comparative case study (Hein et al. 2017). The present assemblage from Olympia and Athens, of the Classical Period as well, thus is expected to provide further information about raw material selection, construction particularly of casting moulds and practical use of the pyrotechnical tools in Olympia and Athens. First results based on the investigations during the ARCHLAB visit at the Rathgen Forschungslabor will be discussed in the present report.

## Studied Material

The material for the present study was selected at the Antikensammlung by Dr. Moritz Kiderlen according to the agreement with Dr. Martin Maischberger. During my visit in Berlin I had the opportunity to meet Dr. Maischberger in person (10<sup>th</sup> July 2018) in order to discuss the sampling of the fragments for further analysis. The studied assemblage comprised two fragments from Athens and seven fragments from Olympia (Table 1). Furthermore, two samples of casting core materials were included, which were recently collected from a bronze sculpture, found in Antequera, Spain. Four further fragments of replicates of casting molds, fabricated by Prof. Gerwulf Schneider during the initial study in the 1980s and stored in the Antikensammlung as well, were not included in the present study though.

| Sample | Site       | Catalogue No | type              | section | powder |
|--------|------------|--------------|-------------------|---------|--------|
| Ker 1  | Kerameikos | 2924         | mold              | 1       | 1      |
| Ker 2  | Kerameikos | 2926         | crucible          | 2       | 1      |
| Oly 1  | Olympia    | 1685         | mold              | 1       | 3      |
| Oly 2  | Olympia    | 1639         | mold              | 1       | 2      |
| Oly 3  | Olympia    | 1647         | mold              | 2       | 2      |
| Oly 4  | Olympia    | 1675         | mold/crucible     | 2       | 3      |
| Oly 5  | Olympia    | 1682         | crucible          | 1       | 1      |
| Oly 6  | Olympia    | 1678         | crucible          | 1       | 1      |
| Oly 7  | Olympia    | 500          | tuyere            | 1       | 1      |
| Ant 1  | Antequera  | no number    | casting core body |         | 1      |
| Ant    | Antequera  | no number    | casting core foot |         | 1      |

Table 1 – Studied material of the Antikensammlung

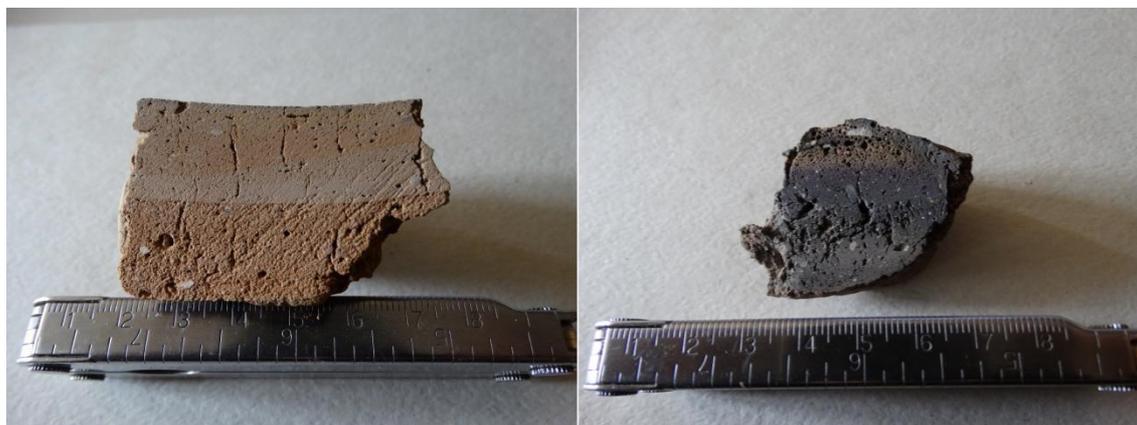


Figure 1 – left: Fragment of a casting mold from Olympia (Oly 1, G 1685) indicating construction of different layers; right: fragment of a crucible from Athens (Ker 2, G 2926)

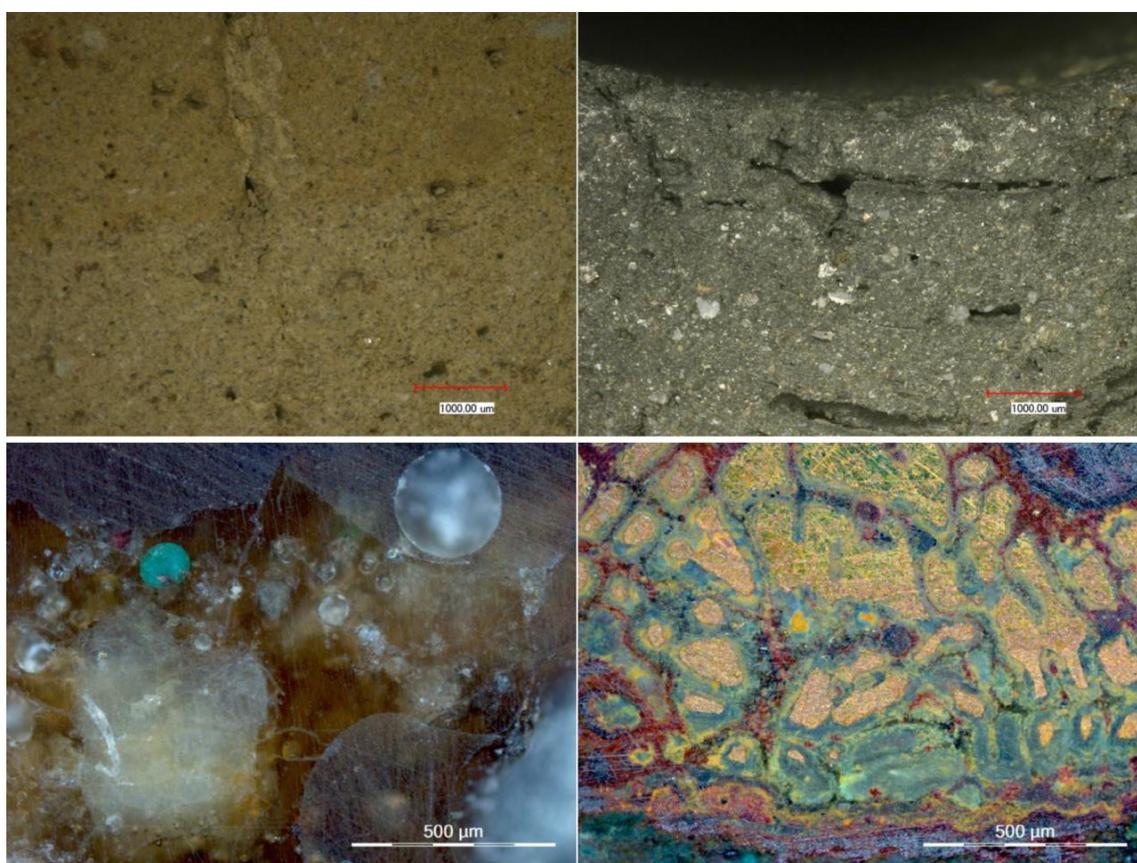
The fragments were first photographed and examined with a handheld USB microscope in low magnification. The investigated mold fragments in particular indicated already by naked eye the use of different raw materials or clay paste mixtures applied in layers on the initial wax model (Fig. 1, left). On the other hand the investigated crucible fragments indicated zones of high vitrification or even slags, evidencing clearly the high temperatures affecting the internal layers (Fig. 1, right).

## Sampling and sample preparation

According to the agreement with Dr. Maischberger small samples were taken along the sections of the fragments from Athens and Olympia using a small diamond cutting wheel. The samples were taken parallel to the originally cut sections, remaining from the sampling in the 1980s and they had a thickness of c. 1 to 2 mm. Some of the larger fragments were not sampled over the entire section. Part of each sample (c. 0.2 g) was powdered for further analysis with FTIR and neutron activation analysis (NAA). Of the casting core materials only powders were collected as they did not show any interpretable structure. The sections were embedded in resin and polished after hardening.

## Analytical Examination

### *Optical microscopy*



*Figure 2 – top left: Micrograph of a casting mold from Olympia (Oly 1, G 1685) indicating the layered construction with different clay pastes; top right: Micrograph of a casting mold from Athens (Ker 1, G 2924) presenting large voids and cracks parallel to the surface; bottom left: Micrograph of a fragment of a crucible from Athens (Ker 2, G 2926) presenting a copper prill; bottom right: Micrograph of a fragment of a crucible from Olympia (Oly 5, G 1682) presenting a copper inclusion.*

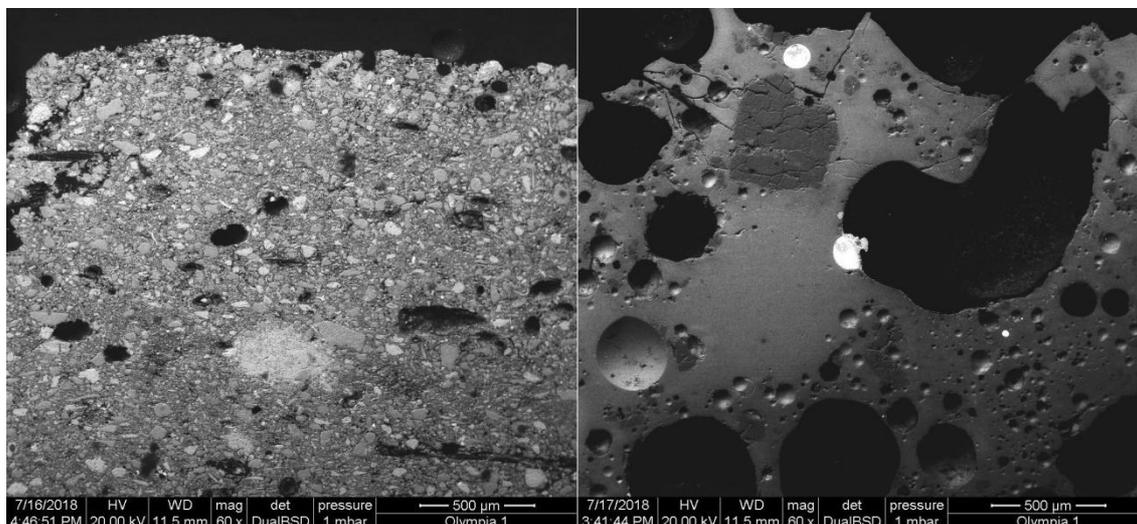
The cut sections of the original samples and the polished sections, prepared during the ARCHLB Visit, were first examined under the optical microscope. Scope of this examination was an initial characterization of the fabrics and pore structures, identification of potential

temper materials added to the clay paste and the investigation of the construction of the ceramics and particularly the molds in layers. Furthermore, in the case of the crucibles metallic remains were identified providing information about the metallurgical process.

#### *Scanning electron microscopy (SEM)*

Polished sections of the ceramics were investigated by SEM, using a FEI Quanta 200 SEM. The samples were examined in low vacuum using backscattering mode focusing at first on the pore structure, which in former studies has proven to be a decisive technological parameter in the fabrication and function of pyrotechnical ceramics (Hein and Kilikoglou 2007, Evely et al. 2012, Hein et al. 2013). Sample Oly 1 (Fig. 3, left), fragment of a mold from Olympia, presented clear evidence of organic fibres which had been initially added to the clay paste leaving extended pores parallel to the internal surface after firing of the molds. Sample Ker 2 (Fig. 3, right), fragment of a crucible from Athens, on the other hand presented a slagged internal surface including copper prills, evidencing the processing of the metal inside the crucible and the reaction of the ceramics with the melting load.

The SEM examination of all prepared sections is planned to be continued in high vacuum. Among other aspects, this will allow for examining the ceramics in higher magnification in secondary electron mode in order to investigate the micromorphology of the ceramics in different layers of molds and crucibles. The degree of vitrification in particular will allow for assessing the temperatures the ceramics were exposed to and the heat transfer during use.



*Figure 3 – left: SEM micrograph in backscattering mode of a section of a casting mold from Olympia (Oly 1, G 1685) presenting the characteristic pore structure of the internal layer; right: SEM micrograph in backscattering mode of a section of a crucible from Athens (Ker 2, G 2926) presenting the slagged internal surface with large bloating pores and prills of the processed metals.*

#### *Fourier-Transform Infrared Spectroscopy (FTIR)*

Sub-samples of the seventeen powdered samples were prepared for FTIR. For this they were mixed with KBr in a ratio of 1.2:100 (3 mg:250 mg) and pressed to pills with a diameter of

10mm. These pills were investigated with a Perkin-Elmer PARAGON 1000 PC FTIR Spectrometer in a range of 4000 to 500  $\text{cm}^{-1}$ .

The FTIR spectra indicated clear differences between molds and crucibles particularly in terms of the presence or absence of bands which are associated with  $\text{CO}_3$  (1429–1434, 875 and 714  $\text{cm}^{-1}$ ). In the case of the mold Oly 1 (Fig. 4, left) all 3 layers presented strong  $\text{CO}_3$  bands, indicating that the maximum temperatures reached in the mold did not exceed the temperature necessary for decarbonisation (above c. 850 °C) or at least did not exceed it for a sufficient time period. Also the broad absorption bands around 3620  $\text{cm}^{-1}$  indicate the presence of clay-bound hydroxyls and thus comparatively low temperature not sufficient for the complete decomposition of the clay minerals. However, the variation of intensity of this absorption as well as the shift of the main Si-O band at frequencies of 1060–1070  $\text{cm}^{-1}$  towards higher frequencies indicate temperature differences in the different layers.

The FTIR spectra of the investigated crucibles on the other hand indicated essentially higher temperatures the ceramics were exposed to. The absence of  $\text{CO}_3$  bands especially in the ceramics from Athens, furthermore, indicate the use of low calcareous clays, preventing also the recarbonisation after use.

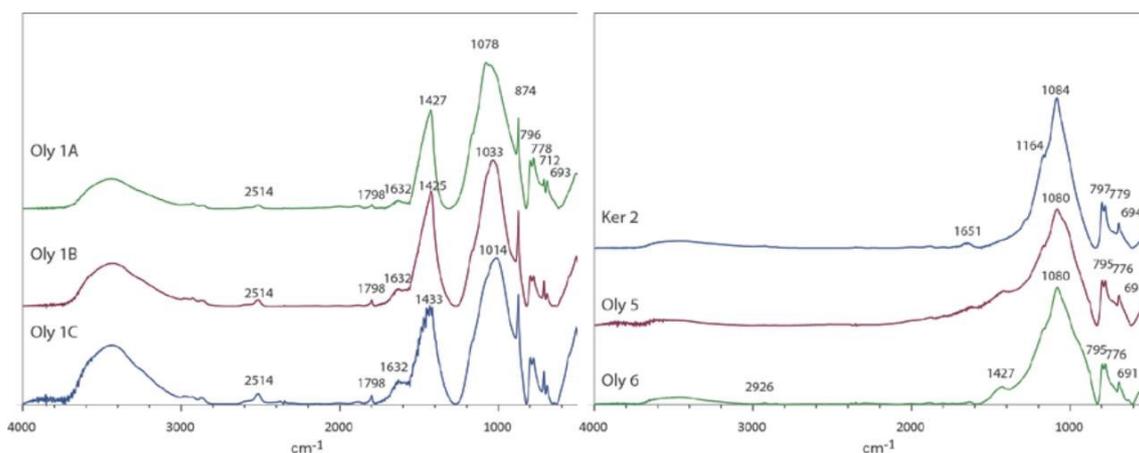


Figure 4 – left: FTIR spectra of the three ceramic layers of a casting mold from Olympia (Oly 1, G 1685); right: FTIR spectra of a crucible from Athens (Ker 2, G 2926) and two crucibles from Olympia (Oly 5, G 1682; Oly 6, G 1678).

### Raman microscopy

The potential of Raman microscopy in the investigation of pyrotechnical ceramics was tested with the section of Sample Olympia 1. This attempt was focused on possible distinction of specific iron oxides and the identification of other characteristic non-plastic inclusions. The achieved preliminary results, though, indicated that Raman microscopy is not suitable in the initial analytical approach but rather as a potential complementary method to answer specific questions emerging during an investigation with other analytical methods. Thus, the investigation with Raman microscopy was ceased at the present stage and will be continued rather in the future course of the present project.

## Conclusions

The ARCHLAB Visit at the Rathgen Forschungslabor provided the opportunity for a first examination of the original materials, excavated in the 1980s, and sampling for complementary analytical examinations, part of which could be already carried out during the course of the laboratory visit. Particularly the SEM investigation is expected to provide new information about the construction of the pyrotechnical ceramics and about technology, concerning ceramics as well as metal casting. Even though the ceramics have been already examined in former studies new aspects, such as a new interpretation of the role of organic tempering and an assessment of heat transfer in the different types of ceramics, will contribute to the understanding of function and use of pyrotechnical ceramics during the Classical Period. The results will be investigated in a larger chronological context of the research of casting technologies, from the Bronze Age, over Iron Age and Archaic until the Hellenistic and Roman Period.

The study will be continued and completed at N.C.S.R. "Demokritos". Furthermore, powdered samples will be analyzed with NAA for their trace element composition in collaboration Dr. H. Mommsen (University of Bonn). Thus, reference data for the different clay pastes used for the construction of pyrotechnical ceramics in Olympia and Athens will be generated and included in a publicly available database.

## Publication Plans

The results of the present project are planned to be published as article in a peer reviewed journal, such as *Archaeometry*, *Journal of Archaeological Science* or *Archaeological and Anthropological Science*. Because the results of the NAA should be included, which will be available at earliest by the end of this year or begin of next year, a manuscript can be finalized probably by next year. Apart from a journal publication, the presentation of the study results in combination with other research on casting ceramics are planned to be presented at the conference *Archaeometallurgy in Europe V*, which will be held in Miskolc, Hungary next year.

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