In archaeological research the existence of a pottery workshop of Archaic Samian decorated fine ware is controversial discussed, especially after the recent results from Miletus, which point to a special primacy of Milesian workshops. Up to now, there have been only insufficient chemical analyses of supposedly Samian and undoubtedly Samian pottery from Samos itself, which are of substantial importance to clarify this problem. The publication of the pottery found in the excavations of Hans Walter in the early layers of the Heraion of Samos by Wolf-Dietrich and Barbara Niemeier (Samos 21,2) was taken as an opportunity to carry out these analyses. Since the majority of the vessels in question are unique objects of high-quality that cannot be sampled with the invasive NAA method, the non-invasive pXRF method was chosen.
In March 2023 an assemblage of 313 ceramic fragments and vessels from the Heraion Sanctuary in Samos was analyzed for their elemental composition using portable energy-dispersive XRF (pXRF). The major part of the ceramics was located in the storerooms of the Heraion excavation while 61 objects were analyzed in the Archaeological Museum of Vathy and one Fikellura Amphora in the Archaeological Museum of Pythagorion.

The pXRF measurements were carried out using a NITON XL3t GOLDD+ handheld system. For the present study the preset ‘soil’ method was used, which had been already successfully tested for ceramic analyses. The life time of each measurement, which was carried out in air, was 120 seconds, measuring in three energy ranges. Without using vacuum or helium flow, concentrations of elements with atomic numbers > 16 (sulphur) are reliably determined. During the measurement the system was placed in a stand looking upwards and the samples were placed on top. The measurement area had an estimated diameter of c. 6 millimeters and a photograph of each area was recorded with the integrated camera. The analytical method was completely non-destructive and non-invasive. It has to be considered though that XRF is a highly surface sensitive method, so that surface areas were selected, which appeared to be clear from deterioration or encrustation, ideally broken sections or flaked surfaces with exposed clay/ceramic body. Some of the samples were analysed in two or three areas in order to assess the variation of the pXRF results, when measuring the same sample. Thus, finally 384 individual measurements were taken of the present assemblage of clay sealings. The composition will be given as elemental concentrations in ppm (µg/g) as mainly minor or trace elements were measured with the present ‘soil’ method. Of the 33 elements, compositions of which were determined, 23 elements presented considerable numbers of concentrations above the lower limit of detection (> LOD): S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Rb, Sr, Zr, Sn, Sb, Te, Cs, Ba, Pb, Th and U. For statistical evaluation the element concentrations were normalized by log-ratio transformation.
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The study uncovered an elemental cluster of 250 of the sampled objects that can be addressed as Samian and clearly distinguishes itself from the elemental composition of the ceramics of other East Aegean production centres. This cluster can be subdivided into further subclusters that can be arranged chronologically.
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