

Chemical composition of archaeological ceramics from Roman and other periods in Central Europe

Abstract

During forty years of research on archaeological ceramics, a large series of chemical analyses using WD-XRF has been carried out alongside thin-section studies and MGR-analyses. This part of our databank deals with data collated from the Roman provinces, mainly in Central Europe at sites in Germania Superior, Germania Inferior, Belgica, Raetia and some sites in Gallia, Noricum, Pannonia, and the Barbaricum. Some earlier and later ceramics are also included. The original aim of the project was to establish reference groups for provenance studies using chemical analysis.

Description

The starting point at the Arbeitsgruppe Archäometrie, Freie Universität Berlin, was a research project called "Material und Herstellungstechnik antiker Fundstücke", financed by the German Volkswagenstiftung from 1973 to 1977. Ceramics and raw materials of the Roman pottery manufacturing centre Rheinzabern were studied in detail to test the possibilities of laboratory pottery analysis (Schneider 1978). Samples for the study were also available from recent excavations in which the Arbeitsgruppe had participated. Samplings of clay raw materials from the region between Strasbourg and Mainz were included. Alteration effects detected in ceramics depending on the composition of their depositional environment were also studied using chemical analysis and experiments.

The aim of subsequent work was to determine reference groups for the Roman production of terra sigillata, common wares, and bricks in the Roman provinces north of the Alps ("Atlas ortsspezifischer Zusammensetzungen von Keramik"). Pottery from some sites in Gaul, Noricum and Pannonia, as well as from Neolithic and medieval contexts and from the Barbaricum is included here; however, numerous chemical data for Roman terracotta figurines and bricks, Italian sigillata imports, and medieval pottery are not included. The same is true of pottery from Italian sites, the Mediterranean, the Black Sea region and the Near East, which will be presented in following parts of the databank. Data was exchanged with archaeometric labs in Fribourg (Marino Maggetti) and Lyon (Maurice Picon), where the same chemical analysis method (WD-XRF) is used, as a means of control to our data. The analysis results of the three labs proved to be comparable, and recent analyses have also shown that the long-term precision of the data produced in Berlin is guaranteed (M. Daszkiewicz, G. Schneider, P. Kögler, *Forum Archaeologiae – Zeitschrift für klassische Archäologie* 83 / VI / 2017, <http://farch.net/forum0617/83analyse.html>). The collation of data was not systematic but depended on actual archaeological research projects. For the Roman pottery of Xanten, Frankfurt and Mainz the analyses were done as part of doctoral theses, including the practical work of the responsible archaeologist in the lab. In all cases, the research group worked closely with the archaeologists at the sites, who were involved in the discussion of the questions and the selection of samples for analysis, as well as in the final interpretation.

The data were clustered and reference groups were defined using archaeological criteria, thin-section studies and, after 1994, also matrix classification by refiring (MGR-analysis) and technological studies. Regardless of where the sherds had been found, all samples attributed to a chemically homogeneous group were deemed to represent a chemical reference group with or without a secure geographical attribution. Details given in the descriptions of the samples are much less perfect than they should be, but some more information may be found in the publications.

Remarks on the columns

All samples are unequivocally identified by their lab.-nos. Chemical reference groups are based on multivariate interpretation of chemical data and have been discussed in the publications listed in the column source. Nevertheless, the attributions are often preliminary or not verified. The columns headed object, object type, ware and stamp provide brief information based on the documentation given by the responsible archaeologist (photographic documentation or drawings, sometimes available, are not included in the databank). This is also the case with the rough dating sometimes given. Site, findspot, museum, and inv.-no.

(find-no., catalogue-no.) are given if available. Coordinates for sites are referenced to the World Geodetic System 1984. The column headed findspot provides details of context, archaeological record number, etc.

Selected publications

G. Schneider, Anwendung quantitativer Materialanalysen auf Herkunftsbestimmungen antiker Keramik, Berliner Beiträge zur Archäometrie 3, 1978, 63-122.

M. Daszkiewicz, G. Schneider, E. Bobryk, Technologische Untersuchungen zur Keramik von Rheinzabern, in: M. Frey und N. Hanel (Hrsg.), Archäologie, Naturwissenschaften, Umwelt. BAR International Series 929, 2001, 59-71.

S. Biegert, B. Liesen, G. Schneider, Keramik-Referenzgruppen römischer Töpfereien in Nieder- und Obergermanien, Berliner Beiträge zur Archäometrie 19, 2002, 5-29.

Research Group in the lab

Gerwulf Schneider, mineralogist/geochemist at Freie Universität Berlin, Arbeitsgruppe Archäometrie, Institut für Anorganische und Analytische Chemie (schnarch3@gmail.com).

From the beginning of the project until about 1990 Heinz Knoll was involved as a chemist, and Bettina Hoffmann and Erwin Wirz as archaeologists. Annette Rother worked in the lab for some time on pottery from Urach and on medieval pottery e.g. Pingsdorfer Ware which is not included here.

After 2003 the Arbeitsgruppe Archäometrie continued to work at Freie Universität Berlin, Excellence Cluster 264-Topoi.

Malgorzata Daszkiewicz, ARCHEA, Warsaw has been part of the team since 1994; since 2003 she has also been affiliated with the Excellence Cluster at Freie Universität Berlin (m.dasz@wp.pl).

The archaeologists Susanne Biegert, Bernd Liesen, Jens Dolata and Alexander Heising worked for some time in the lab of the Arbeitsgruppe preparing their samples for their doctoral thesis. These analyses results are included here but not for a series of around 600 stamped Roman bricks collected for his thesis almost exclusively by Jens Dolata.

Research group and cooperation in the field and in museums

The research group consisted of the numerous archaeologists responsible for their excavations or museums and changed according to the individual projects, working together for anything between a few weeks up to several years.

Applied method of analysis

Samples are prepared by pulverising fragments weighing mostly above two grams, having first removed their surfaces and cleaned the remaining fragments with distilled water in an ultrasonic device. The resulting powders are dried at 105°C and then ignited at 900°C (heating rate 200°C/h, soaking time 1h), melted 1:4 with a lithium-borate mixture (Merck Spectromelt A12) and cast into small discs of 32 mm diameter for measurement. This data, therefore, is valid for ignited samples but, with the losses on ignition given (column LOI), may be recalculated to a dry basis. Because total iron is calculated as Fe₂O₃ losses on ignition of not fully oxidized sherds can be negative. For the major elements the contents of the oxides are normalized to a constant sum of 100%. The last column (SUM) gives the originally measured sum of all oxides.

Initially, measurements were made using a Philips PW1212. From 1980 to 2007 a PW1400 WDXRF-Spectrometer was used. Since 2008 samples have been measured at GeoForschungsZentrum GFZ Potsdam using a PANalytical AXIOS spectrometer (courtesy of Rudolf Naumann and Anja Schleicher). The calibration is based on certified international standard reference samples (CRM's). The precision (coefficient of variation) for major elements is better than 1rel%, and for trace elements this rises up to 20rel% depending on the concentrations. Trace elements with a reduced precision are Cu, Y, Nb, La, Ce, and Pb. Accuracy is tested by analysing more than fifty CRM's and by exchange of samples with other laboratories. Maximum deviations for major and trace elements above 100 ppm are between 5 and 10rel%. The lower limit of detection is about 5 ppm for the analysed trace elements.

In cases where less powder was available (e.g. when samples are obtained by drilling using a tungsten carbide drill), 0.1 g of powdered sample is melted 1:19 with Merck Spectromelt A10 and cast into small discs of 25 mm diameter. The higher dilution reduces the precision for Na and trace elements. Therefore Cu, Y, Nb, La, Ce, Pb are not indicated for 0.1 g samples. The data for the major elements are given as weight percent of the oxides in the usual geochemical order. The data for trace elements are given as ppm ($\mu\text{g/g}$) in the order of atomic numbers. Empty spaces mean "not determined" or unreliable values.

Some remarks on the interpretation of the chemical analyses

The chemical elements differ in significance and should not be treated equally. Most important are the major elements expressed as oxides, which are dictated by the kind of clay and temper (Si, Al, Fe, Ca). This should be the basis of the first grouping. Other major or minor elements may characterize certain provenances (Ti, K, Mg) and are essential in distinguishing groups. Of the trace elements the most useful for distinguishing groups are Cr, Ni, Rb, Sr, Zr, which are determined with great precision. Phosphorus is an important indication of alteration effects. It characterizes weathered sherds, most of which also exhibit higher losses on ignition and/or elevated Ba and/or Sr values. Heavily altered sherds may also be depleted in Rb, K, and Ca. In most cases, strongly elevated values of Cu, Zn and Pb may be due to contamination of the sherds by their burial environment. Mn, V, and Zn may sometimes help to distinguish groups. This is also the case with the less precisely determined traces of Cu, Y, Nb, La, and Ce. The values of Nb, La and Th (as well as the measured but not published values of Co, Ga and Nd) may differ between series due to contamination or calibration problems. Generally, all values below about 20 ppm should be treated with caution. In cases where data for the same sample in different publications deviate to some degree this is due to later repetition of measurements resulting in corrected averages.

Data obtained in other labs may be used when the series of determined major and trace elements and the precision and accuracy with which they were determined are comparable. This is to be checked with data obtained by pXRF (portable energy-dispersive XRF) as also for data obtained by ICP-OES, ICP-MS and NAA.

Institutions

- Freie Universität Berlin, Arbeitsgruppe Archäometrie, Institut für Anorganische und Analytische Chemie (after 2003: Freie Universität Berlin, Arbeitsgruppe Archäometrie, Excellence Cluster 264 Topoi)
- Dr. Małgorzata Daszkiewicz, ARCHEA, Warsaw and Freie Universität Berlin

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Keywords

chemical reference groups, WD-XRF, ceramics, Roman, medieval