Archaeological Ceramics

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Papers presented at a seminar on Ceramics as
Archaeological Material held at the Smithsonian
Institution, Washington, D.C., and the National
Bureau of Standards, Gaithersburg, Maryland,
29 September – 1 October 1980, one of the
Smithsonian Institution / National Bureau of
Standards seminars on the Application of the
Materials and Measurement Sciences to
Archaeology and Museum Conservation organized
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_____. 1966. Die Chemie der Antiken Keramik. *Naturwissenchaften* 53: 218–23.

Kingery, W. D. 1974. A technical characterization of two Cypriot ceramics. In Bishey, A., ed., *Recent Advances in Science and Technology of Materials*, Vol. 3, pp. 169–86. New York: Plenum Publishing Corporation.

Longworth, G., and Warren, S. E. 1975. Mössbauer spectroscopy of Greek "Etruscan" pottery. *Nature* 255: 625–27.

Longworth, G., and Tite, M. S. 1979. Mössbauer studies on the nature of red or black glazes on Greek and Indian painted ware. *Journal de Physique* 40, C2:460–61.

Maniatis, Y., and Tite, M. S. 1978. Examination of Roman and Medieval pottery using the scanning electron microscope. *Acta Praehistorica et Archaeologica* 9/10: 125–30.

Maniatis, Y., and Tite, M. S. 1981. Technological examination of Neolithic-Bronze Age pottery from Central and Southeast Europe and from the Near East. *J. Archaeological Science* 8: 59–76.

Matson, F. R. 1971. A study of temperatures used in firing ancient Mesopotamian pottery. In Brill, R. H., ed., *Science and Archaeology*, pp. 65–79. Cambridge: M.I.T. Press.

Mayes, P. 1961. The firing of a pottery kiln of a Romano-British type at Boston, Lincolnshire. *Archaeometry* 4: 4–30.

_____. 1962. The firing of a second pottery kiln of a Romano-British type at Boston, Lincolnshire. *Archaeometry* 5: 80–92.

Noll, W.; Holm, R.; and Born, L. 1975. Painting of ancient ceramics. *Angewandte Chemie* 14: 602–613.

Peters, T., and Iberg, R. 1978. Mineralogical changes during firing of calcium-rich brick clays. *American Ceramic Society Bulletin* 57: 503–509.

Picon, M.; Vichy, M.; and Meille, E. 1971. Composition of Lezoux, Lyon and Arezzo Samian ware. *Archaeometry* 13: 191–208.

Picon, M., and Vichy, M. 1974. Recherches sur la composition des céramiques de Lyon. *Revue Archeologique de l'Est et du Centre-Est* 25: 37–59.

Sanders, H. P. 1973. Pore size determinations in Neolithic, Iron Age, Roman, and other pottery. *Archaeometry* 15: 159–61.

Schumann, T. 1942. Oberflächenverzierung in der antiben Töpferkunst, Terra Sigillata und Griechische Schwarzrotmalerie. *Berichte Deutscher Keramischen Gesellschaft* 23: 408–426.

Shepard, O. A. 1956. *Ceramics for the archaeologist*, pp. 113–36. Washington, D.C.: Carnegie Institution of Washington.

Tite, M. S. 1969. Determination of the firing temperature of ancient ceramics by measurement of thermal expansion: a reassessment. *Archaeometry* 11: 132–43.

Tite, M. S., and Maniatis, Y. 1975. Examination of ancient pottery using the scanning electron microscope. *Nature* 257: 122–23.

Tite, M. S.; Maniatis, Y.; Meeks, N. D.; Bimson, M.; Hughes, M. J.; and Leppard, S. C. 1979. Technological studies of ancient ceramics. In Wertime, T. A., and Wertime, S. F., eds., *Early Pyrotechnology*. Washington, D.C.: Smithsonian Institution Press, forthcoming [1982].

11. Phase Analysis and Its Significance for Technology and Origin
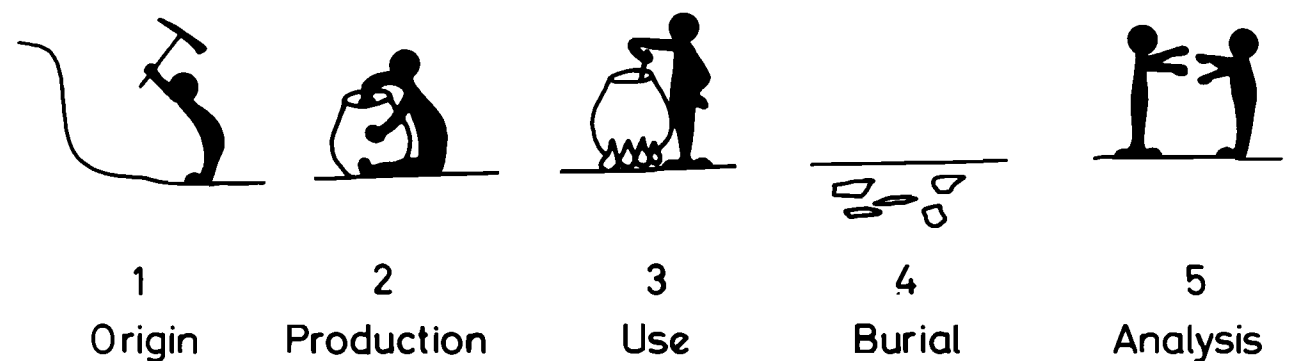
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Abstract

This paper presents the results of investigations on temper, paste, and porosity of ancient ceramics by application of optical microscopy, X-ray diffractometry, and measurement of porosity. Porosity data must be interpreted carefully; the results of controlled firing and refiring of illitic calcareous and kaolinitic noncalcareous clays show how difficult their interpretation in terms of ancient firing temperatures and initial granulometry can be. The effect of reducing atmosphere is also discussed. Much more research work is needed, however, before porosity data can be interpreted correctly. The mineralogical changes during firing of the paste are very useful for an estimation of the ancient firing temperature, the nature of the raw material, the technology of the processing and firing atmosphere. Firing experiments on kaolinitic noncalcareous and illitic calcareous clays are discussed. There is a great need for more detailed research, especially with respect to reducing firing conditions. A review of the mineralogical changes during burial leading to secondary products as calcite, montmorillonite, mixed-layers, and zeolites is presented. Finally, the application of temper analysis for identification of local or foreign production of coarse ware is discussed and arguments for identifying artificially added temper are presented.

Introduction

If an archaeologist gives a sherd to an archaeoceramist for analysis, then the sherd has reached the fifth step of its long life (Fig. 1). These steps are: *(1)* extraction of the clay from a clay pit ("origin"); *(2)* manufacture of the ceramic object (processing, firing); *(3)* use with subsequent breakdown; *(4)* burial stage; and *(5)* analysis. From the first four steps the sherd has stored information and it possesses a memory which can be activated by the analysis (step 5) gaining the "sleeping" information about the steps 1 to 4. This can be done by a lot of physicochemical methods based on the analysis of the chemistry, mineralogy, and other physical parameters as magnetism, thermoluminescence, etc., of the sherd. Considering the *chemical composition*, it is obvious that the chemistry is a function of the composition of the original clay, of its processing (the extraction of coarse particles or addition of temper fragments can change the chemistry), of the use (the chemistry of a cooking pot can be affected by reaction processes between the pot itself and the food), of the burial stage (infiltration of foreign matter in the sherd body, extraction of sherd matter due to solvents from invading solutions) and of the archaeological treatment (cleaning with acids can lead to dissolution of carbonates). Therefore, the chemical analysis *alone* can-

Figure 1. The five steps in the life of a ceramic object and the types of information that can be found using a defined scientific method.
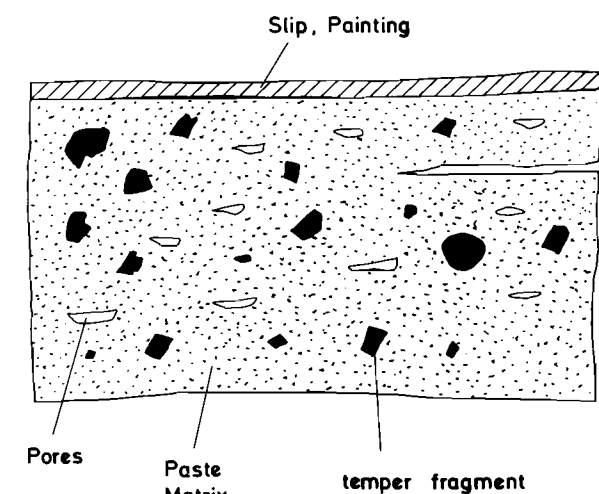

Figure 2. The physical phases of a sherd.

not show which parameter (original clay, processing, use, burial, treatment) affects which chemical element. This can be done by other methods only, involving the physical phases of the sherd: *voids* (pores) and solid *matter* (temper and matrix/paste); *see* Figure 2.

The combination of both *chemical* and *physical analysis* leads to a better understanding of all the factors involved in the long history of an archaeological sherd and is the key to solving archaeological ques-

tions such as: *(a)* origin of temper and matrix (origin of the ceramic body); *(b)* technology of the ceramic process (artificial additions, treatment of the clay, molding, firing, etc.); *(c)* function (use) of the ceramic object; *(d)* age; and *(e)* burial conditions.

This paper will not give a complete review of all methods and applications of phase analysis on ancient ceramics. The aim is to present and discuss some archaeologically important aspects of phase analysis based on the results of recent research of the working group on "Archaeoceramics" from the University of Fribourg (Switzerland). Therefore literature is cited only when needed and the reader interested in other aspects and more information is referred to the papers of Courtois (1976), Farnsworth (1964), Frechen (1972), Peacock (1970), and Shepard (1968).

The following sections deal with the porosity of the ancient sherds and with the mineralogy of paste and temper. To avoid misinterpretation, some general remarks are outlined at the start.

Porosity includes all pores or voids of a sherd and is mainly due to the firing process, the initial porosity, the chemistry/mineralogy of the starting material; by addition of outburning organic substances (e.g., straw), an artificial porosity can be produced (Rye 1976). During use and/or burial the porosity can be affected by cementation (e.g., crystallization of gypsum; Courtois 1976) or leaching processes (calcite

dissolution; Kuepfer and Maggetti 1978; Marro 1978; Rottlaender 1973).

The distinction between *temper* and *paste* (matrix) is based on two criteria: granulometry and the plastic/nonplastic behavior of the initial nonfired material. By definition, temper includes all phases with a diameter greater than 0.015 mm (Maggetti 1979). The matrix predominantly contains the initially plastic phases with minor amounts of nonplastic ones, the temper predominantly nonplastics. Mineralogically, matrix and temper consist of solid phases which can be amorphous or crystalline. The initial plastic phases are sheet silicates (e.g., kaolinite, illite, montmorillonite); the nonplastic phases are either natural rock and/or mineral fragments, natural organic or artificial inorganic materials (e.g., fired brick). The temper can be added artificially (artificial temper) or was present in the initial clay (natural temper).

From the genetic point of view the solid phases can be classified into three groups: *(1)* primary or prefiring minerals (relictic minerals inherited from the initial clay); *(2)* firing minerals (formed during the firing process); and *(3)* secondary minerals (postfiring minerals, formed during the use or the burial stage).

The Interpretation of Porosity Data

Quantitative analyses of porosity include the measurement of specific and apparent weight, the pore size distribution, and the subsequent calculation of total open and closed porosity as well as the specific surface. Only few people have used these parameters for studies on archaeological ceramic objects (Cabotse 1964; Heimann 1976, 1977; Sanders 1973; Strunk-Lichtenberg et al. 1973). The porosity depends on many factors. According to Maggetti and Kahr (1980) the following parameters are important: mineralogical composition of the clay, chemical composition of the clay, granulometry of the clay, firing temperature, firing atmosphere, processing of the clay, and burial changes (interaction of the sherd and invading solutions resulting in cementation or dissolution).

An example of the application of simple measurements of specific and apparent weight for technological purposes is given by the paper of Beckmann et al. (1971). In this paper the increase of the apparent weight of medieval ceramics from Siegburg from 1,62 g/cm³ (1150 A.D., earthenware) to 2,35 g/cm³ (1450 A.D., stoneware) is clearly related to an evolution in ceramic technology. The paper also discusses other porosity parameters such as open porosity, total porosity, and so on. The changes of porosity with increasing firing temperatures could in principle be used for the estimation of ancient firing temperatures. This will now be reviewed critically.

Porosity of Kaolinitic Noncalcareous Clays

The work of Maggetti and Rossmanith (1981) on fourteen kaolinitic clays (noncalcareous) showed the importance of *granulometry* and *firing temperature* on porosity data, the former being the decisive one (Figs. 3–7). It can be inferred from this study that for
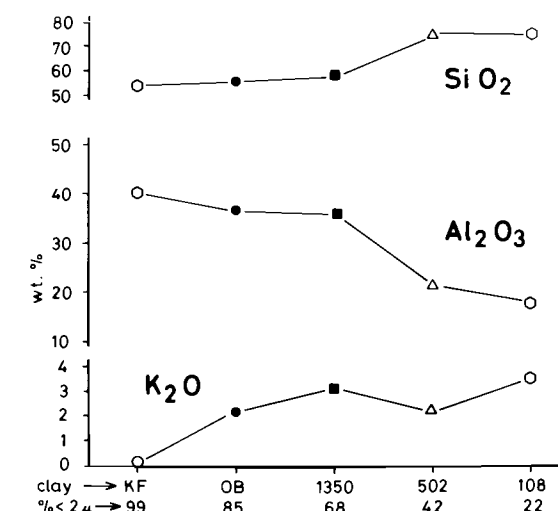

Figure 3. Granulometry: SiO_2, Al_2O_3, and K_2O content of five kaolinitic noncalcareous clays (nos. KF, OB, 1350, 502, and 108).
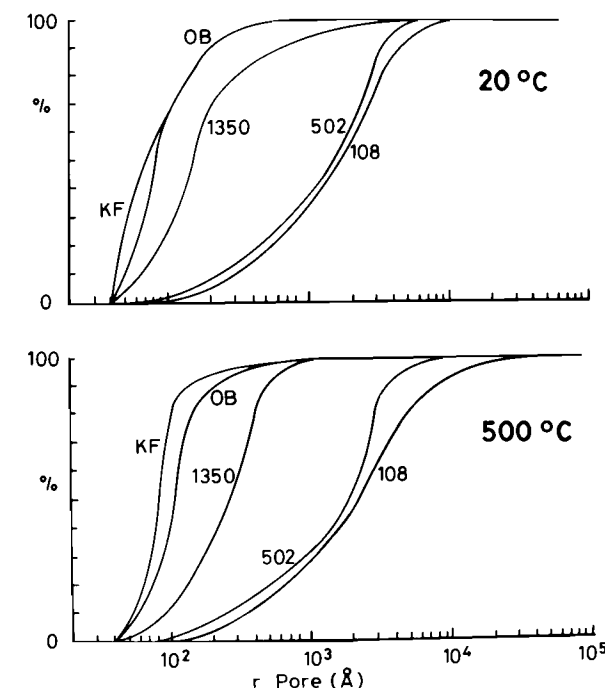

Figure 4. Pore size distribution curves (PSDC) of the clays from Figure 3 at room temperature and 500°C. The fine grained clays have markedly finer pores than the coarse grained ones and their PSDC are much steeper.
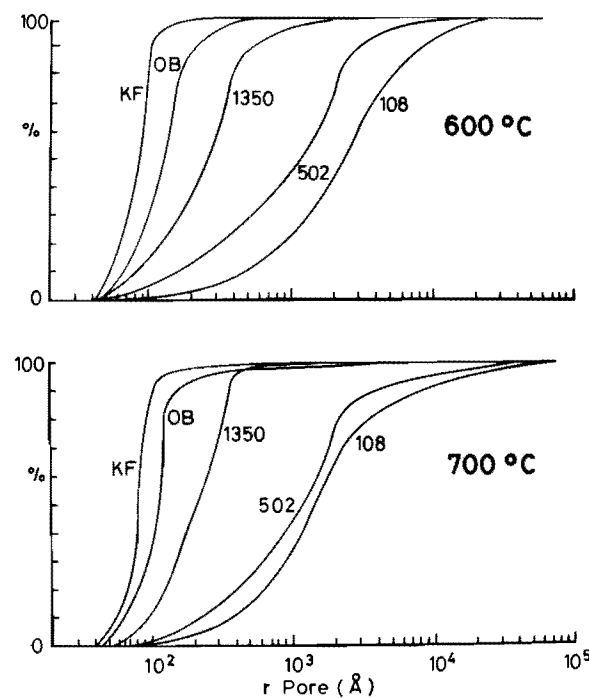
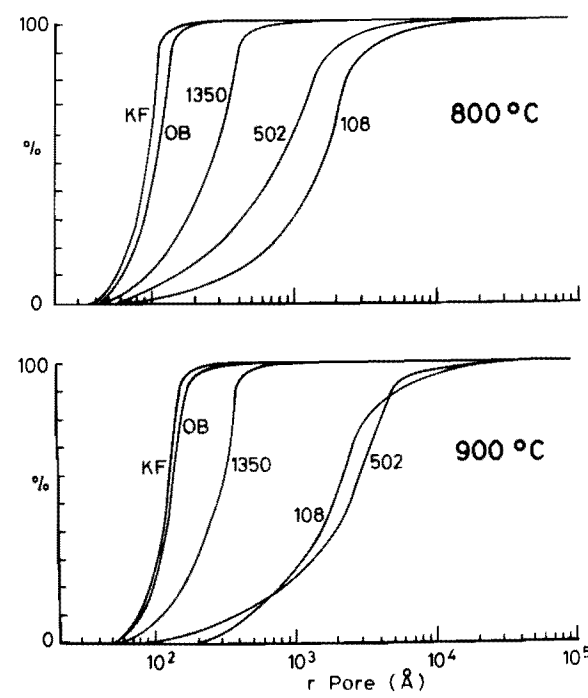Figure 5. PSDC of the clays from Figure 3 at 600°C and 700°C.

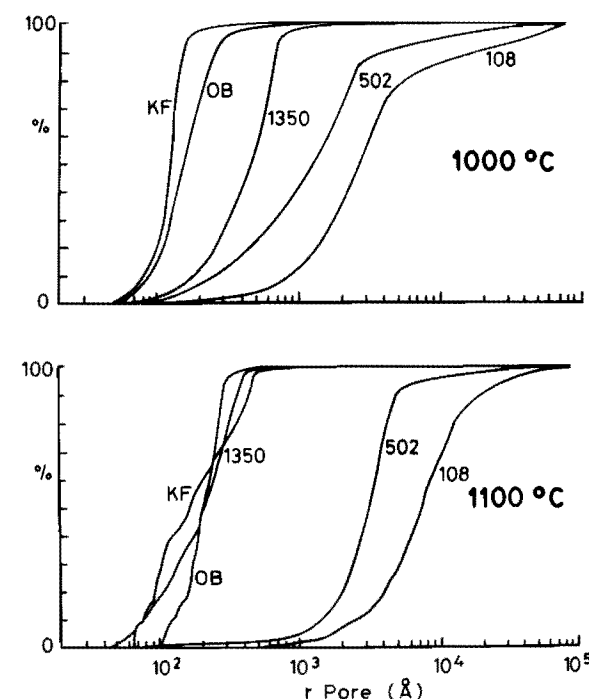Figure 6. PSDC of the clays from Figure 3 at 800°C and 900°C.

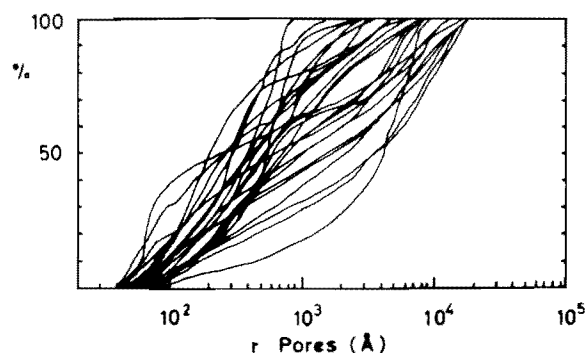Figure 7. PSDC of the clays from Figure 3 at 1000°C and 1100°C.

Figure 8. PSDC of Iron Age sherds from the Heuneburg, Germany (Maggetti and Galetti 1980). The curves are steep or lesser inclined, indicating the existence of two sherd populations. Since the chemical compositions of the two populations are identical, the differences in the PSDC can be explained by different granulometry of the raw materials (n = 25).

a given firing temperature and a known chemical or mineralogical composition of two ceramic objects, the differences in porosity data — especially the pore size distribution curves — can be explained by different granulometric composition of the starting materials; fine grained clays have steeper pore size distribution curves (PSDC) than the coarser grained
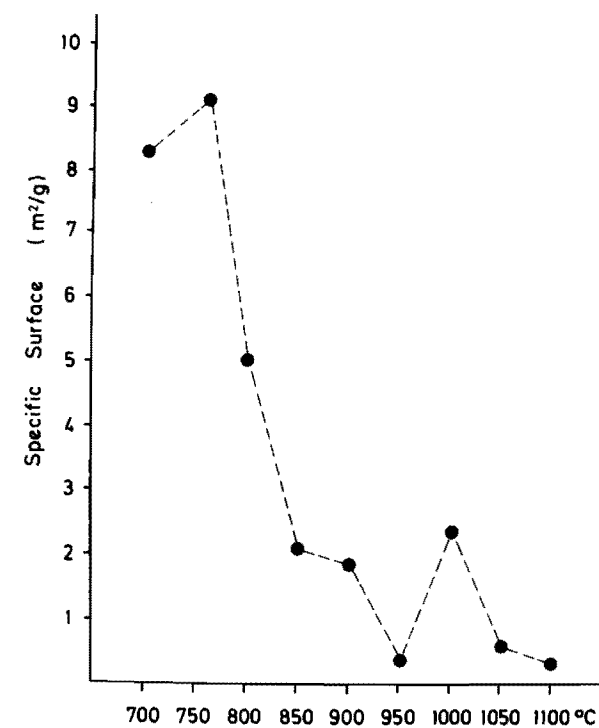

Figure 9. Variation of the specific surface of an illitic calcareous clay with firing temperature. The specific surface generally decreases with increasing firing temperature.

ones. This result was used by Maggetti and Schwab (1982) to explain differences in PSDC of Iron Age sherds from the same locality and the same chemical/mineralogical composition as a function of differing granulometry. These differences could be due to differing original clay or to differing treatment of the material before firing (Fig. 8).

A second result of the cited work on kaolinitic clays is the hypothesis that it would be likely that by refiring of pieces of a kaolinitic archaeological object at different temperatures (say 600°, 700°, 800°C, etc.) the porosity changes could be used to find out the original firing temperature. However, this hypothesis has not been tested by experimental refiring of modern samples with known previous firing temperature.

Porosity of Illitic Calcareous Clays

As in the case of the kaolinitic clays (with exceptions; see Maggetti and Rossmanith 1981), illitic calcareous clays show considerable porosity changes with increasing firing temperature. These changes are mainly due to sintering phenomena as well as crystallization of new firing minerals. As an example the behavior of the illitic calcareous clay from La Péniche (Switzerland) is shown in Figure 9. The chemical composition is given in Table 1. With increasing fir-

Table 1. Chemical analysis of an illitic calcareous clay (no. LP 142, Maggetti 1981)

SiO_2 (wt %)	55.83	Ba (ppm)	409
TiO_2	0.67	Cr	68
Al_2O_3	16.78	Cu	37
Fe_{tot} as Fe_2O_3	5.63	Ni	74
MnO	0.09	Rb	127
MgO	2.77	Sr	235
CaO	13.53	Zn	98
Na_2O	1.07	Zr	116
K_2O	3.36		
P_2O_5	0.21		
	99.94		

loss by ignition (1100°C) 13.14 wt. %

ing temperature the specific surface diminishes and the mean diameter of the pores increases in general, both phenomena being explained by sintering processes leading to a closure of the micropores. The reason why the sample 1000°C does not follow the general trend is not well understood. The open microporosity and the shape of the pore size distribution curves (PSDC) are not much affected by the firing temperature.

The more or less regular decrease of the specific surface and increase of the mean pore radii (Fig. 10) lead to the hypothesis that a refiring of an object with known firing temperature would not change its mean pore size and its specific surface at refiring temperatures below the original firing temperature, but would change it at refiring temperatures higher then the original firing temperature. If this assumption is correct, then the unknown original firing temperature of an ancient object could be inferred by refiring some portions of it and determining at which temperature the mean pore radii increase and the specific surface decreases (with respect to the parameters of the starting material). This temperature should be higher than the original firing temperature. In order to test this hypothesis, experimental refiring of previously heated (800°, 900°, 1000°C) clay samples LP 142 were performed. The refiring temperatures were lower and higher than the original firing temperature, the atmosphere was oxidizing, and the samples were held 1 hour at maximum temperature in an electric furnace. The results are summarized in Table 2 and can be interpreted as follows:

(1) Refiring temperatures below the original firing temperature: The mean pore radius as well as the specific surface are not identical to the one of the start-
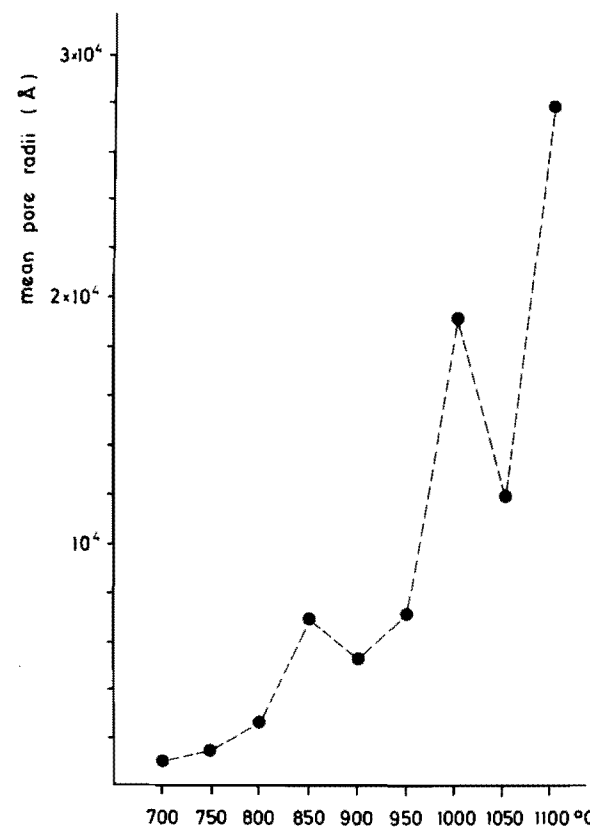
Marino Maggetti

Figure 10. Variation of the radii of the pores of an illitic calcareous clay with firing temperature. A general increase of the pores with increasing firing temperature is to be seen.

Table 2. Refiring of three fired (800°, 900°, 1000°C) illitic calcareous clay samples (LP₀ 142). Specific surface (m²/g) and mean pore radii (Å).

Firing temperature: 800°C

	800	750	800	850	900	950°C
m²/g	5.09	4.47	2.59	1.75	2.10	1.64
Å	2600	2000	2300	4200	3800	3000

Firing temperature: 900°C

	900	800	850	900	950	1000	1050°C
m²/g	1.93	2.78	2.79	2.06	1.99	1.03	0.93
Å	5500	2600	2600	3000	3200	3900	26'000

Firing temperature: 1000°C

	1000	800	900	950	1000	1050°C
m²/g	2.40	1.78	1.56	1.64	2.45	1.44
Å	19'000	3600	2900	3100	3000	3600

ing material; they can be higher or lower.

(2) Refiring temperatures above the original firing temperature: Both parameters follow the trend of the LP 142, with exception of the refired 800°C sample.

(3) If the values of the starting material are compared with the ones from the refired specimens, no reliable extrapolation to the original firing temperature can be made based on both parameters.

In conclusion the promising hypothesis is to be abandoned, at least for the studied calcareous illitic clay. It seems that no reliable original firing temperature estimation can be made by refiring experiments and subsequent porosity analyses.

The Influence of Firing Atmosphere

Experimental work on the influence of a reducing atmosphere on porosity data of fired clays is very scarce. Heimann et al. (1980) studied one single calcareous illitic clay: the samples show a strong correlation between apparent weight and open porosity. The apparent weight as well as the mean pore radius increases, and the open porosity decreases with increasing firing temperature. These phenomena are explained by sintering processes which are stronger at higher oxygen fugacities ($fO_2 > 10^{-4}$atm).

Conclusion

The application of porosity data in archaeoceramic research is surely very useful, but must be done with caution, because many factors are involved. At present, more experimental work is urgently needed on kaolinitic, illitic, montmorillonitic (calcareous and noncalcareous clays) in oxidizing and reducing atmosphere. This is the only way to understand and interpret porosity data correctly.

Paste Analysis

In our research, the paste is studied by optical microscopy (polarizing petrographic microscope), differential thermal analysis (DTA), and X-ray diffraction techniques. These methods yield data on texture and mineralogy of the paste which can be interpreted with regard to the origin of the clay, ceramic technique, firing temperatures, firing atmosphere, and burial conditions. Among others, the following authors successfully used paste analysis: Isphording (1974); Isphording and Wilson (1974).

Nature of the Initial Clay

The fact that the ancient potters used differing clays at the same site has been recognized by Maggetti (1979), Nungaesser and Maggetti (1978), and Maggetti and Schwab (1982) by identification of the mineralogical composition of low fired sherds. These sherds can be classified — with respect to the presence or absence of carbonatic minerals — into
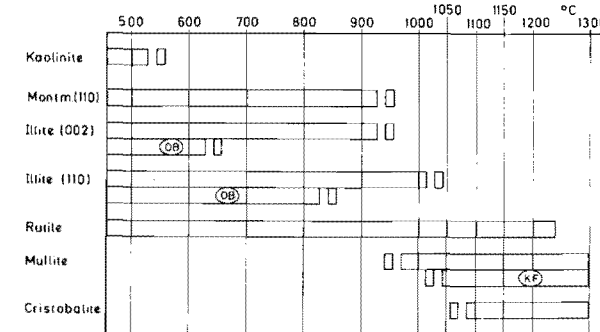

Figure 11. Stability of minerals in five kaolinitic noncalcareous clays during controlled firing; (110) and (002) are selected reflections.
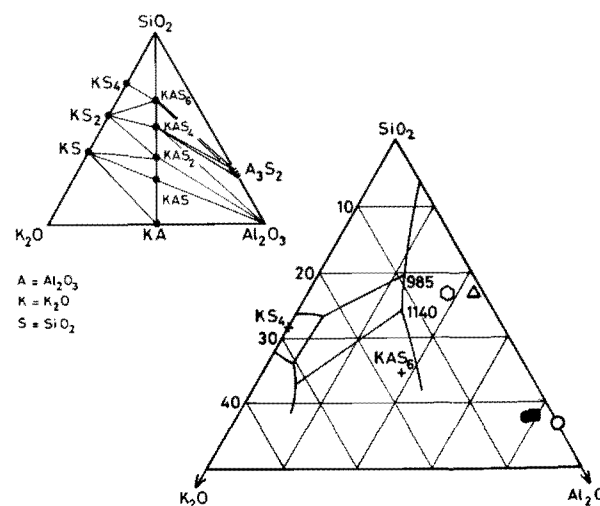

Figure 12. Position of five kaolinitic noncalcareous clays (see Fig. 3) in the SiO_2, K_2O, Al_2O_3 diagram. LEFT: possible subsolidus relations. RIGHT: liquidus relations.
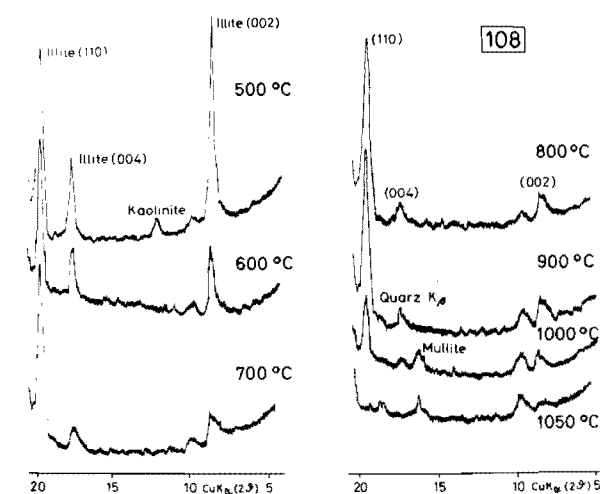

Figure 13. Kaolinitic noncalcareous clay no. 108: changes of intensity of illite basal reflections (002, 004) with increasing firing temperature.

three main groups: *(a)* sherds with carbonatic matrix; *(b)* sherds with silicatic matrix; and *(c)* sherds with carbonatic-silicatic matrix. In these sherds the firing temperatures were estimated not to have exceeded 600°-700°C; so the carbonates and silicates are mostly primary minerals and the differing mineralogical compositions of the pastes are therefore due to the use of marly clays (calcareous clays), moderately calcareous clays, or noncalcareous clays. Additionally, the textural features of these three clays give indications if a starting clay was well or poorly processed (Maggetti 1979).

Firing Temperatures

The firing temperature of an ancient sherd can be estimated by various approaches using the mineralogical changes occurring during a controlled refiring of the sherd itself and comparison of the transformations with the starting materials, or by refiring of an identical clay and comparison of the results obtained on the ancient sherd with those obtained on the clay. The changes in mineralogical composition of various clays dependent on the firing temperature were studied by many workers. An excellent review is given by Grim (1968).

The refiring experiments (Fig. 11) on five *noncalcareous kaolinitic clays* from the Westerwald region (Maggetti and Rossmanith 1981) shows the breakdown of kaolinite between 500°-600°C; the basal reflections of illite are stable up to 900°-1000°C, the (110) reflections to 1000°-1050°C. Rutile is stable up to 1200°C and probably dissolves in the glassy phase at higher temperatures. (Fig. 12). These observations are in good agreement with those of other authors. Kaolinitic clays therefore seem to be not so useful for archaeothermometric purposes since no pronounced mineralogical changes occur between 600°-1000°C. However, if a 2M illite is present, additional information can be gained. As shown by Figure 13, the intensity of the basal reflection of illite decreases with increasing firing temperature; in contrast the (110) reflection is not essentially affected below 900°-950°C. Therefore the ratio (height of the 002-peak/height of the 110-peak) of illite can be used for temperature calibration in the range of 500°-950°C. For the considered clay 108, this ratio is greater than 0.3 for temperatures below 600°C and lies between 0.2-0.1 for temperatures between 600°-950°C. Another ratio can close up the temperature estimation; Figure 14 gives an example for two clays showing the decrease of the ratio (height of the peak 110/half height width of the peak 110) with increasing firing temperatures. It seems plausible that by refiring kaolinitic objects containing 2M illites, a rough estimation of the ancient firing temperature (under
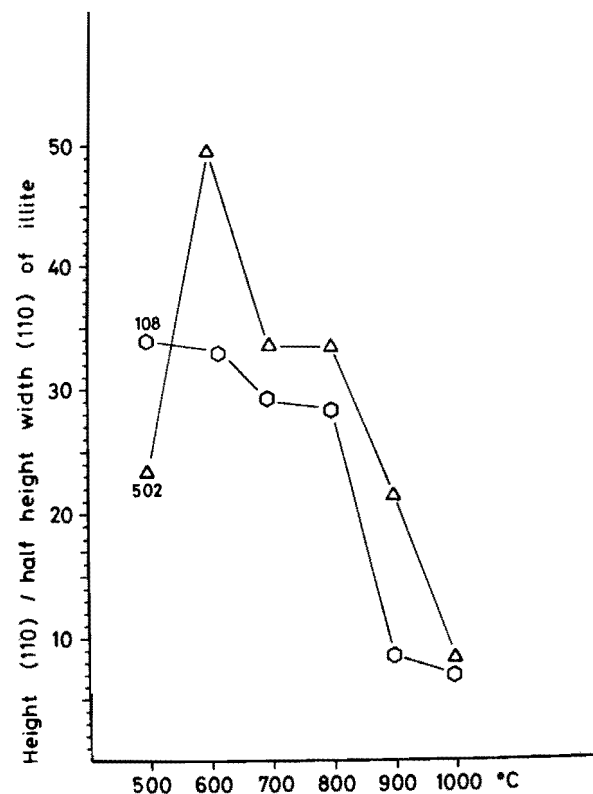
Figure 14. Kaolinitic noncalcareous clays no. 108 and 502. Variation of the ratio: height of (110)-peak/half height width (110)-peak of illite with firing temperature.
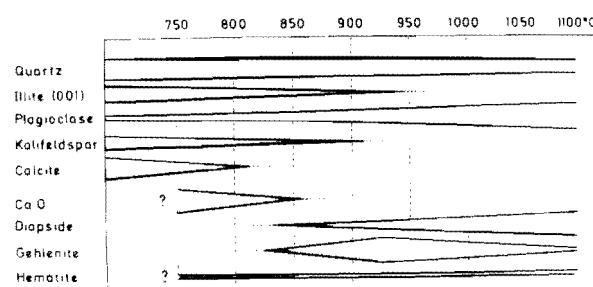

Figure 15. Mineralogical changes during firing of illitic calcareous clays.

oxidizing conditions) is possible.

The firing experiments carried out on *illitic calcareous and noncalcareous clays* yielded very useful information. The calcareous illitic clays are ideal for archaeothermometric purposes because of the important mineralogical transformations during firing. Figure 15 summarizes the experiments of Peters and Jenny (1973); Peters and Iberg (1978); Kuepfer and Maggetti (1978); and Maggetti (1981). It shows that calcite decomposes at 750°-800°C in a natural clay and that calcium-silicates (gehlenite, diopside/wollastonite, plagioclase) appear in the range
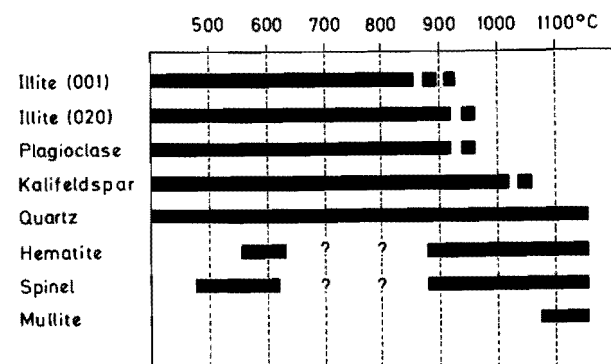

Figure 16. Mineralogical changes during firing of illitic noncalcareous clays.

850°-900°C. The so-called gehlenite problem (absence or presence of gehlenite) was studied by Heimann and Maggetti (1981) and Maggetti and Heimann (1979); these studies showed that the absence of the gehlenite phase is due to three possible reasons: *(a)* fine-grained initial clay; *(b)* decomposition of gehlenite to various secondary minerals during the burial stage (especially zeolites and calcite); or *(c)* very high firing temperatures or very long holding at maximum temperatures. It seems that the first point is the controlling factor, but the exact relations to granulometry are still unknown.

The noncalcareous illitic clays do not show so spectacular changes in mineralogy as the calcareous one (Fig. 16) and therefore mineralogical analysis of the paste is not very useful for archaeothermometry.

Firing Atmosphere

Up to now all cited experiments were carried out under oxidizing conditions. But what about mineralogical changes of the matrix in a reducing firing atmosphere? In this context very little information can be found in literature. Heimann and coworkers (1980) have shown that a calcareous illitic clay yields differing paragenesis for differing reducing conditions:

(a) $fO_2 < 10^{-4}$ atm, 1000°C
sanidine + magnetite + ferro-cordierite + biotite + fayalite + quartz + plagioclase
(b) $fO_2 \ 10^{-4}$ to 2.10^{-1} atm, 1000°C
sanidine + magnetite + tridymite + quartz + plagioclase.

Up to now no author has noticed the presence of ferro-cordierite in a black or grayish calcareous illitic sherd. So the assumption suggests itself that the oxy-

gen fugacity of the ancient kilns was greater than 10^{-4} atm. However, much more basic work is needed, because Maggetti et al. (1981) inferred from the coexistence of two Fe-spinels (magnetite$_{ss}$ + hercynite$_{ss}$) in black coatings of campanian sherds that the fO_2 was between 10^{-12} and 10^{-21}! The starting material of these coatings was most probably a very fine grained, noncalcareous, and highly ferrous illitic clay suspension.

Mineralogical Changes during Burial

Fired ceramic bodies are very sensitive to environmental conditions, especially low fired sherds (500°-700°C) which react with invading solutions. The following reaction processes can be listed: extraction of sherd material (dissolution phenomena); deposition of minerals in pores and voids (cementation phenomena); and decomposition of existing primary or firing minerals to secondary minerals. The secondary products are mostly carbonates (calcite), hydrates (hydration of hematite to goethite: Enriquez et al. 1979), hydrosilicates (zeolites, clay minerals), and sulfates (gypsum: Courtois 1976).

Secondary calcite is clearly identifiable if present in high fired products (e.g., terra sigillata which was fired between 900°-1000°C) or in pores (Courtois 1976; Kuepfer and Maggetti 1978). The origin of this calcite can be either completely allochthonous (crystallization directly from invading, carbonatic solutions without contribution of matter from the sherd itself) or partly allochthonous (crystallization of secondary minerals by reaction between existing minerals in the sherd and invading solutions). An example for the latter case is the reaction of gehlenite + solutions to secondary calcite, which was postulated by Kuepfer and Maggetti (1978) for the explanation of the presence of calcite and the absence of gehlenite in high fired terra sigillata sherds. This reaction was successfully performed in experiments by Heimann and Maggetti (1980).

Rehydration of incompletely destroyed clay minerals in low fired sherds is another possible process and was noticed by several authors (Courtois 1973; Noll 1977; Maggetti and Schwab 1982; Nungaesser and Maggetti 1978, 1981). Regarding montmorillonite the secondary nature of this mineral is obvious, since montmorillonite and/or mixed layer minerals containing a smectite phase lose the water layer between the silicate units below 300°C, the sherds having been fired at temperatures of 500°-600°C; however X-ray diffractograms of low fired sherds frequently show a large peak between 5°-10°2θ (for CuK$_\alpha$ radiation) — see Figure 17. In some cases this peak represents mixed-layer phases containing montmorillonite, as detected by the glycolation technique. In other cases,
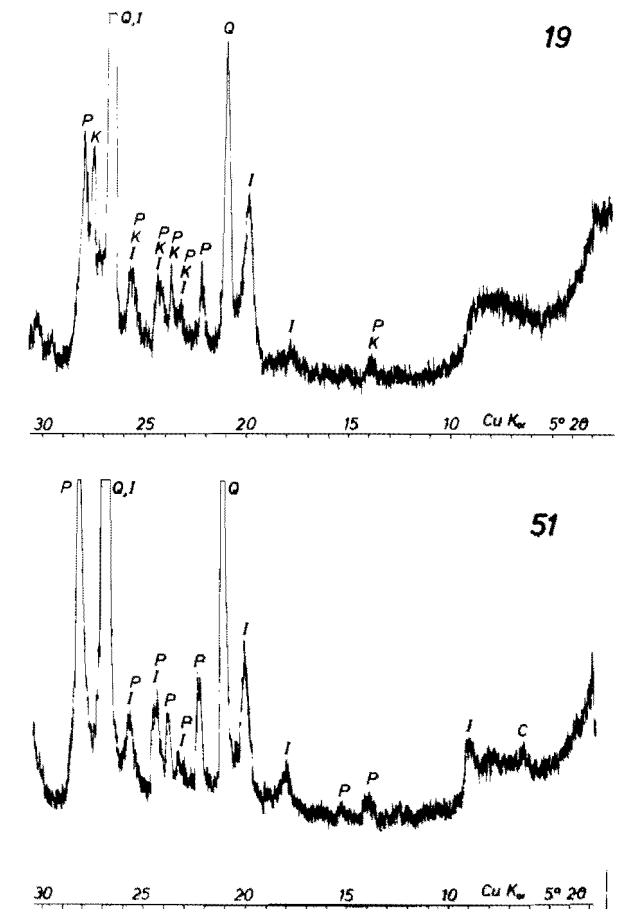

Figure 17. X-ray diffractogram of two neolithic sherds (nos. 19 and 51) from the Burgäschisee, Switzerland (Nungaesser and Maggetti 1978). C = chlorite, I = illite, K = kalifeldspar, P = plagioclase, Q = quartz. The large peak between 5 and 10°2θ is due to rehydration during burial of clay minerals which were partially destroyed by firing.

however, the large peak shows no variation by glycolation but is reduced by firing at 200°-300°C to a single illite peak or split into an illite + chlorite basal peak. It must therefore be assumed that the large peak is caused by the presence of very fine grained clay particles of a mixed layer type (probably chlorite-illite), all particles having different chemical compositions and being poorly crystalline. The disappearance of these large peaks by firing above 300°C is an indication that these mixed layers were formed during burial.

Conclusion

The previous sections have shown how useful paste analysis can be for archaeological questions; however, as in the case for porosity, more basic research on various types of clays with varying firing atmosphere is needed. Only by this approach can the technology of reduced fired gray or black ware be fully understood.
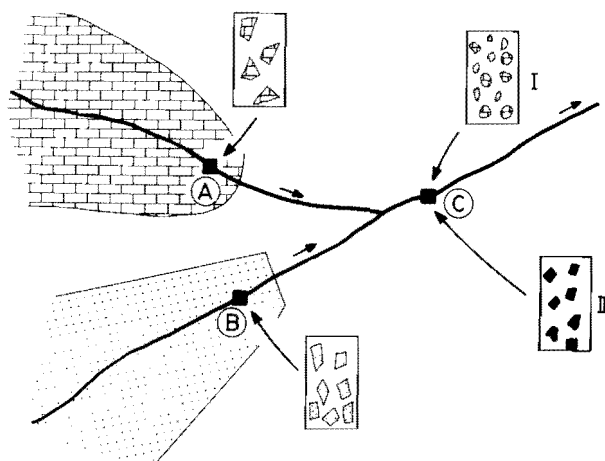
Figure 18. Principle of source localization of the temper fragments by petrographic analysis. [See text for explanation.]

Temper Analysis

The use of temper analysis (by optical microscopy) to identify local or foreign production of a ceramic object is a powerful method especially for coarse grained sherds. Additionally, morphological criteria can be used for technological aspects, e.g., to find out whether or not a certain temper has been added artificially to a clay during processing. In the following section a discussion of these two applications is presented.

Importation or Local Production

The analysis and identification of temper for product localization has been the object of many studies (e.g., Arnold 1972; Aumassip et al. 1969; Frechen 1958; Hays and Hassan 1974; Koehler and Morton 1954; Lais 1957; Maggetti et al. 1979; Maggetti and Galetti 1980; Marro et al. 1979; Nungaesser and Maggetti 1978; Okrusch et al. 1973; Peacock 1967, 1970; Schmid 1966; Slatkine 1972; Stauffer et al. 1979; Williams 1979). The method is based on the assumption that a potter uses local material for tempering his clay. This assumption has been corroborated by ethnological studies. The temper of a local pottery must therefore reflect the geology of the site; an imported vessel can be recognized if it contains a temper not found in the neighborhood. The approach is made in two steps: (1) identification of the temper; and (2) comparison of the nature of the temper fragments with local geology and subsequent establishment if the temper in the sherd can be from a local source or not.

A schematic explanation is given with the aid of the sketch in Figure 18 which shows two rivers and three archaeological sites (A, B, C). Rectangular diagrams represent schematic thin sections of ceramic objects with schematic temper fragments found at each site. The local geology of site A is dominated by one single rock type, for instance granite. A local potter will use local material for his pottery; the temper will therefore consist of fragments of granite or fragments of mineral derived from weathered granite. If the microscopical analysis of a sherd from station A reveals the presence of granite or granitic minerals, a local production of this object would be highly probable.

The thin section of the ceramic ware from site B contains temper fragments of material (say limestone) found at or in the vicinity of the station. Here, too, a local production is probable based on the possible derivation of the temper fragments from local rocks. At the station C, two sherds were analyzed. The sherd number I contains temper fragments of granite and limestone, whose outcrops are found upstream; fluvial transport has rounded these fragments and reduced their grain size. The temper of this sherd can easily be explained by the local geology. The ceramic body could therefore be of local production. In contrast, the sherd number II has rock fragments (e.g., basalt) as characteristic temper which are not to be found in the local or upstream geology. This sherd cannot have been produced locally and must therefore be imported. A local production of the ceramic with use of imported temper is theoretically possible, but has not been recorded by ethnological research work until now.

Artificial Temper

Adding artificial temper is a common practice among ancient potters. An artificial temper can readily be identified in the following cases:

(1) Calcite fragments. The presence of fresh rhomboedric calcite crush fragments with angular, sharp outlines is possible only if the ancient potters used crushed calcite; naturally present calcite would be very fine grained owing to the splitting behavior of calcite and would also have rounded edges because of transport by water during the deposition of the clay.

(2) Fired brick. Fired brick, too, is an indication of artificially added temper and can be recognized — with respect to the embedding sherd — by differing color, mineralogical composition, or texture (Maggetti 1979).

(3) Organic material. Addition of straw, etc., was also frequently used by ancient potters and can be identified by the presence of an abnormally high and coarse porosity and/or relicts of the organic matter, often as black carbonaceous substance.
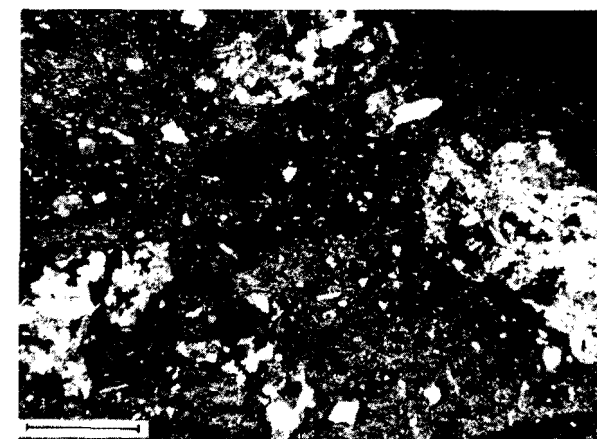

Figure 19. Angular gneissic temper fragments in a thin section of a Bronze Age sherd from Montlingerberg, Switzerland (Marro 1978; Marro et al. 1979). Sample Me 24, crossed polars, bar = 1 mm.
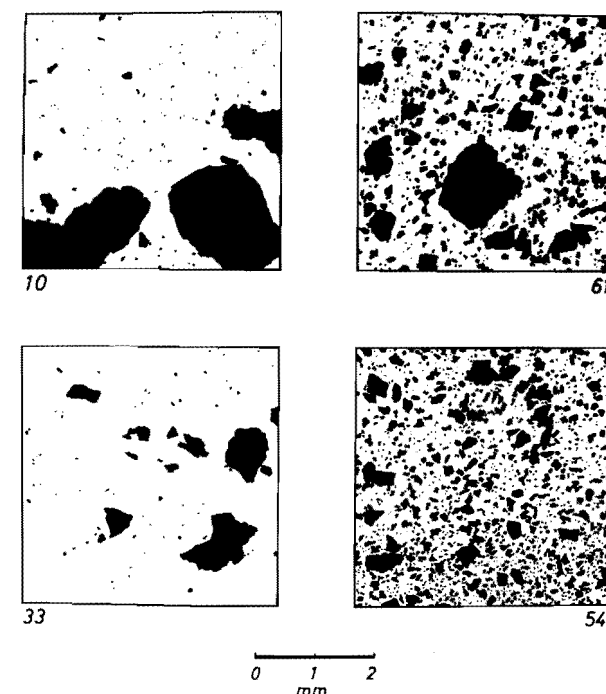

Figure 20. Four thin sections of neolithic pottery from the Burgäschisee, Switzerland. The nos. 10, 33, and 61 show — with respect to the grain size of the temper fragments — two populations, a fine grained one and a coarse grained, the latter having sharp edges and representing therefore crushed rock fragments. These fragments were added artificially to a natural fine grained temper.

(4) Shape of the fragments. Angular fragments with sharp edges are often an indication that crushed material has been used (Marro 1978); see Figure 19. However, regarding finer grained particles the naturally present quartz grains in some alpine clays have angular shapes, too! This is due to the fact that a short distance of transport does not allow a rounding of the grains.

(5) Granulometry. The presence of two populations of grain sizes (the so-called hiatal structure) is also an indication that the coarser particles were added artificially (Figure 20; Nungaesser and Maggetti 1978).

Conclusion

Chemical analysis is a very powerful method for identifying the origin of an ancient object, but it must not be forgotten that the actually analyzed chemical data are a function of many processes affecting the chemistry of the original clay (e.g., processing, tempering, firing, use, burial, cleaning of the object). These aspects can be elucidated by the phase analysis based on the identification of the mineralogical nature of temper and paste, their texture, the porosity, and other physical parameters. The phase analysis can be used, too, for localization in suitable cases, as for coarse ceramics. But the most important application is the elucidation of ancient technology. Actually, the method suffers some severe limitations, since fundamental basic research is still lacking. Much more work on typical, widely used clays (calcareous and noncalcareous illitic, montmorillonitic, kaolinitic clays with varying granulometry) at different firing temperatures and atmospheres is needed urgently. Only then can the technology of, for instance, the "reduced" grayish and black ware be understood.

References

Arnold, D. E. 1972. Mineralogical analyses of ceramic materials from Quinua, Department of Ayacucho, Peru. *Archaeometry* 14, 1:93-102.

Aumassip, G.; Marmier, F.; and Trecolle, G. 1969. Dégraissants et forme des poteries. *Libyca A.P.E.* 17: 267-69.

Beckmann, B.; Strunk-Lichtenberg, G.; and Heide, H. 1971. Die frühe Siegburger Keramik und ihre Entwicklung zum Steinzeug. Naturwissenschaftliche Analysen zur Geschichte der mittelalterlichen Keramik. *Keramische Zeitschrift* 23: 656-59.

Cabotse, Jean. 1964. Essai d'application d'un test physique à l'étude de la céramique antique. *Revue archéologique de l'Est et du Centre-Est*, 358-67.

Courtois, L. C. 1973. Phénomènes de "régénération" après cuisson de certaines céramiques anciennes. *Comptes Rendus de l'Académie des Sciences*, Paris. Série D, 276: 2931-33.

_____. 1976. Examen au microscope pétrographique des céramiques archéologiques. *Notes et Monographies Techniques*, no. 8. Centre de recherches archéologiques.

Enriquez, C. R.; Danon, J.; and Beltrao, M. 1979. Differential thermal analysis of some amazonian archaeological pottery. *Archaeometry* 21, 2: 183-86.

Farnsworth, M. 1964. Greek pottery: a mineralogical study. *American Journal of Archaeology* 68: 221-28.

Frechen, J. 1958. Die petrographische Untersuchung der Keramik. In K. Böhner, *Die fränkischen Altertümer des Trierer Landes*, 63-68.

_____. 1972. Petrographische Untersuchungen an römischer Keramik aus Neuss. In Filtzinger, P., ed., *Die röm. Keramik aus dem Militärbereich von Novaesium*. Novaesium V = Limesforschungen Bd. 11: 41-45.

Grim, Ralph E. 1968. *Clay mineralogy*. 2d ed. New York: McGraw Hill.

Hays, T. R., and Hassan, F. A. 1974. Mineralogical analysis of Sudanese neolithic ceramics. *Archaeometry* 16, 1: 71-79.

Heimann, R. 1976. Moderne Poren- und Gefügeuntersuchungen an Keramik. *Informationsblätter zu Nachbarwissenschaften*, Petrographie 7.2: 1-2; 16.

_____. 1977. Korrelation von Porenkenngrössen und chemischer Zusammensetzung von Provinzialrömischer Keramik. In Hennicke, H. W., ed., *Mineralische Rohstoffe als kulturhistorische Informationsquelle*: 234-48. Hagen: Verlag des Vereins Deutscher Emailfachleute.

_____. 1978/79. Mineralogische Vorgänge beim Brennen von Keramik und Archaeothermometrie. *Acta Praehistorica et Archaeologica* 9/10: 79-102.

_____; Maggetti, M.; and Einfalt, H. C. 1980. Zum Verhalten des Eisens beim Brennen eines kalkhaltigen illitischen Tones unter reduzierenden Bedingungen. *Berichte der Deutschen Keramischen Gesellschaft* 57, 6-8: 145-52.

_____, and Maggetti, M. 1981. Experiments on simulated burial of calcareous terra sigillata (mineralogical changes). *British Museum Occasional Paper*, 19: 163-77.

Isphording, W. C. 1974. Combined thermal and X-ray diffraction technique for identification of ceramicware temper and paste minerals. *American Antiquity* 39: 477-83.

_____, and Wilson, E. M. 1974. The relationship of "volcanic ash," SAK LU'UM, and palygorskite in northern Yucatan Maya ceramics. *American Antiquity* 39, 3: 483-88.

Koehler, A., and Morton, F. 1954. Mineralogische Untersuchung prähistorischer Keramik aus Hallstatt im Zusammenhang mit der Frage nach ihrer Herkunft. *Germania* 32: 66-72.

Kuepfer, T., and Maggetti, M. 1978. Die Terra Sigillata von La Péniche (Vidy/Lausanne). *Schweizerische Mineralogische und Petrographische Mitteilungen* 58: 189-212.

Lais, R. 1957. Ein keramischer Brauch im Breisgau des frühen Mittelalters. *Schau-ins-Land* 75: 157-66. Freiburg im Breisgau: Jahresheft des Breisgau-Geschichtsvereins.

Maggetti, Marino. 1979. Mineralogisch-petrographische Untersuchung des Scherbenmaterials der urnenfelderzeitlichen Siedlung Elchinger Kreuz, Landkreis Neu-Ulm/Donau. München: *Kataloge der Prähistorischen Staatssammlung* 19: 141-67.

_____, and Heimann, R. 1979. Bildung und Stabilität von Gehlenit in römischer Feinkeramik. *Schweizerische Mineralogische und Petrographische Mitteilungen*, 59, 3: 413-17.

_____; Marro, C.; and Perini, R. 1979. Risultati delle analisi mineralogiche-petrografiche della ceramica "Luco." *Studi trentini di scienze storiche* LVIII 1: 3-19.

_____. 1981. Composition of Roman pottery from Lausanne (Switzerland). *British Museum Occasional Paper*, 19: 33-49.

_____, and Galetti, G. 1980. Composition of Iron Age fine ceramics from Châtillon-s-Glâne (Kanton Fribourg, Switzerland) and the Heuneburg (Kr. Sigmaringen, West Germany). *Journal of Archaeological Science* 7: 87-91.

_____, and Kahr, G. 1980. Homogenität archäologischer keramischer Objekte: Teil I. Porosität und Porenradienverteilung. *Archäologie und Naturwissenschaften* 2: 1-20.

_____, and Rossmanith, M. 1981. Archaeothermometry of kaolinitic clays. *Revue d'Archéometrie*, III: 185-94.

_____, and Schwab, H. 1982. Iron Age fine pottery from Châtillon-s-Glâne and the Heuneburg. *Archaeometry*, 24, 1: 21-36.

_____; Galetti, G.; Schwander, H.; Picon, M.; and Wessicken, R. 1981. Campanian pottery: the nature of black coatings. *Archaeometry*, 23, 2: 199-208.

Marro, Christian. 1978. Recherches en archéocéramiques. Diplomarbeit, Universität Fribourg.

_____; Maggetti, M.; Stauffer, L.; and Primas, M. 1979. Mineralogisch-petrographische Untersuchungen an Laugener Keramik — ein Beitrag zum Keramikimport im alpinen Raum. *Archäologisches Korrespondenzblatt* 9, 4: 393-400.

Noll, W. 1977. Hallstattzeitliche Keramik der Heuneburg an der oberen Donau. *Archäologie und Naturwissenschaften* 1: 1-19.

Nungaesser, Wolfgang, and Maggetti, Marino. 1978. Mineralogisch-petrographische Untersuchung der neolithischen Töpferware vom Burgäschisee. *Bulletin Société Fribourgeoise des Sciences Naturelles* 67, 2: 152-73.

_____, and Maggetti, Marino. 1981. Etude minéralogique et petrographique de la poterie néolithique du Burgäschisee (suisse). *Revue d'Archéométrie*, III: 225-26.

Okrusch, M.; Strunk-Lichtenberg, G.; and Gabriel, B. 1973. Vorgeschichtliche Keramik aus dem Tibesti (Sahara). I. Das Rohmaterial. *Berichte der Deutschen Keramischen Gesellschaft* 50, 8: 261-67.

Peacock, D. P. S. 1967. The heavy mineral analysis of pottery: a preliminary report. *Archaeometry* 10: 97-100.

_____. 1970. The scientific analysis of ancient ceramics: a review. *World Archaeology* 1: 375-89.

Peters, T., and Jenny, J. P. 1973. Mineralogische Untersuchungen über das Brennverhalten von Ziegeltonen. *Beiträge zur Geologie der Schweiz*, Geotechnische Serie, 50: 1-59.

_____, and Iberg, R. 1978. Mineralogical changes during firing of calcium-rich brick clays. *American Ceramic Society Bulletin* 57, 5: 503-506.

Rottlaender, R., and Schröter, R. 1973. Magerungseffekte an Schussenrieder Gefässen von Riedschachen. *Archaeologisches Korrespondenzblatt* 3, 5: 177-79.

Rye, O. S. 1976. Keeping your temper under control: Materials and the manufacture of Papuan pottery. *Archaeological and Physical Anthropology in Oceania* XI, 2: 106-137.

Sanders, H. P. 1973. Pore-size distribution determinations in Neolithic, Iron Age, Roman and other pottery. *Archaeometry* 15, 1: 159-61.

Schmid, Elisabeth. 1966. Ton und Magerung urgeschichtlicher Keramik vom Schönberg, Gemeinde Ebringen, Landkreis Freiburg. *Mitteilungen des badischen Landesvereins für Naturkunde und Naturschutz*, new series 9, 2: 325-28.

Shepard, A. O. 1968. *Ceramics for the archaeologist*. 5th ed. Washington, D.C.: Carnegie Institution.

Slatkine, A. 1972. Comparative petrographic study of ancient pottery sherds from Israel. *Museum Haaretz Yearbook* 15/16: 101-111.

Stauffer, L.; Maggetti, M.; and Marro, C. 1979. Formenwandel und Produktion der alpinen Laugener Keramik. *Archäologie der Schweiz* 2: 130-37.

Strunk-Lichtenberg, G.; Gabriel, B.; and Okrusch, M. 1973. Vorgeschichtliche Keramik aus dem Tibesti (Sahara). II. Technologischer Entwicklungsstand. *Berichte der Deutschen Keramischen Gesellschaft* 50, 8: 294-99.

Williams, D. F. 1979. Petrological analysis of some mica-dusted and "London ware" pottery. In Shelton, H., ed., *Excavations in Southwark, 1972-1974*, forthcoming.