APPENDIX III
EXAMINATION OF LBK POTSHERDS FROM HIENHEIM

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INTRODUCTION

The examination relates to four LBK potsherds from the excavation "am Weinberg" near Hienheim, Ldkr Kelheim, Bayern. The excavation was carried out by a team of the Institute of Prehistory of the University of Leiden, under the direction of Prof. Dr. P.J.R. Modderman. The four potsherds come from a pit which is filled with dirty loess. The finds from this pit bear the number 325.

The description of the potsherds, according to the system used by the Institute of Prehistory, is given in table 18. It is by J.J. Assendorp. The description demonstrates that the potsherds are tempered with sand and pottery fragments; number WR 75/45 has a comparatively coarse temper with particle sizes up to 2 mm.

METHODS

A thin section was taken from the potsherds for microscopic analysis. A piece of the potsherd was ground. A part of this powder was used for chemical analysis, another part for X-ray diffraction analysis, and a third part for thermal analysis. Besides, test briquettes were fired of four clay samples from the direct vicinity of the excavation, which seemed to have good properties for the freehand forming of pottery. These clays are: loam from the decalcified illuviation zone in the loess (B2t), loam from the calcareous horizon in the loess (C2), a river loam from the valley of the Donau, and a white loam from the Hienheimer Forst. The test briquettes were fired with the purpose to verify whether the clays are suitable for making pottery. The first and the third clay indeed appeared to be suitable at temperatures up to circa 1000° C. Higher temperatures were not considered. At low temperatures, the calcareous loess gives a ceramic product that crumbles and cracks when moistened. The white loam shows so much shrinkage that this material must be considered unfit.

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Table 18. Description of the sherds.

find number	*analysis number*	*temper*				*thickness*	*colour and decoration*	
		sand grains size in mm		*pottery fragments size in mm*				
		< 1	1–2	< 1	1–2			
325–1	WR 75–42	x	–	X	–	4 mm	ext. surface	dark non oxidized
							core	light non oxidized
							int. surface	dark non oxidized
							decorated	
325–6	WR 75–43	X	x	–	–	6–7 mm	ext. surface	dark non oxidized
							core	dark non oxidized
							int. surface	dark non oxidized
							decorated	
325–11	WR 75–44	x	–	x	–	10 mm	ext. surface	light uncertain
							core	dark non oxidized
							int. surface	dark non oxidized
325–14	WR 75–45	X	X	x	X	8 mm	ext. surface	dark non oxidized
							core	dark uncertain
							int. surface	dark non oxidized

temper: X = main component
x = accessory material

colours based on the Munsell system
light = values 6–8
dark = values 2–5
non oxidized = chroma 1
uncertain = chroma 2–5, hue yellower than 2.5 YR

RESULTS OF THE ANALYSIS OF THIN SECTIONS

The results of the analysis of thin sections make it plausible that for the temper of the four potsherds, use was made of the same type of sand, namely a sand with a felspar content of circa 20%. An attempt to determine the degree of temper by means of microscopic analysis with the point counter provided the four figures of table 19.

Table 19. Temper of the potsherd in % of weight.

	WR 75/42	*WR 75/43*	*WR 75/44*	*WR 75/45*
quartz	17	16	23	24
felspar	4	3	5	6

The values mentioned in the table must be regarded with some reserve, because the thin sections of the potsherds have numerous small pores and it is not quite certain whether these were present from the outset or whether part of them originated as a result of the grinding off of quartz and felspar grains. The latter may occur in spite of the fact that the potsherds were impregnated with a synthetic resin before the grinding.

The temper is more clearly visible in the coarse potsherds than in the finer ones; use was made of a sand fraction with grains of up to 0.2 mm. In the finer material of potsherd WR 75/42, a very fine temper occurs with particles between 0.02 and 0.04 mm. This does not mean that the potsherds do not contain coarser grains now and then. The limits given here apply to the greater part of the grains observed in the thin section.

In addition to felspar, the sands used contain a small amount of chert fragments. It can further be said about the temper that the grains are sharp and angular. This could indicate that man obtained the tempering material by pulverizing or calcinating a solid rock.

The temper with pottery fragments mentioned in table 18 can also be observed in the thin sections. As far as temper is concerned, the fragments do not distinguish themselves from the fabric in which they were used.

Finally must be mentioned that one potsherd, namely WR 75/42, is different from the others in that its mass is microscopically rich in coarser micas (0.03 mm). It is not clear whether these belong to the body clay or to the temper.

RESULTS OF THE CHEMICAL ANALYSIS

The chemical analyses are XRF (X-ray fluorescence spectrometry) analyses. The results are given in table 20a.

As far as the results regarding the potsherds are concerned, it may be observed that the values stated want some correction, for it has been proved that the potsherds, during the long period that they were buried in the soil, absorbed clay minerals in their pores because of illuviation by soil development. This can be observed in the thin sections. However, the analysis results were not corrected for this illuviation, because no quantitative methods have been developed yet to do so in an acceptable way. But it appears from the X-ray diffraction analysis that the clay illuviation is about equally important in the four potsherds.

In one respect, the chemical composition of the four potsherds is notably different from the three clay samples (the white loam was left out of consideration), in that the P_2O_5 contents of the potsherds were much higher than those of the clay samples. This might be attributed to the fact that the potsherds come from an environment of dirty loess. The loess filling of the LBK pits has indeed a higher P_2O_5 content than the undisturbed loess. The P_2O_5 content of the latter (fertilized arable) lies between 0.13 and 0.21% with an average of 0.15 (based on 5 measurements by H. v.d. Wetering). The pit fillings have a P_2O_5 content of 0.16–0.27% with an average of 0.23%. The contents in the potsherds are thus even higher.

Furthermore it is notable that the potsherds have a much lower CaO content than the calcareous loess (C2). This makes it improbable that the calcareous loess was used as material for making pottery.

The oxides, as given in table 20a, were converted into a best-fitting mineral composition: a "norm". The calculating procedure is defined generally as a "petrochemical calculating method based on the use of equivalents" (Burri 1959). Table 20b includes the first step from the procedure followed. Table 20c gives a ceramic variant of the norm, which is applicable to coarse ceramic products which are fired at temperatures between 900° C and 1030° C. For the calculating method we refer to v.d. Plas and v. Schuylenborg 1970. The variant starts from the following phases: felspars, wollastonite, hematite, mullite, cordierite, forsterite and quartz. A composition on the basis of these phases offers a better possibility of comparison than one on the basis of oxides. To illustrate this, one may compare the quartz contents from table 20c with the SiO_2 contents from table 20a.

The figures in table 20c show that the quartz contents of the four potsherds are different. The highest

Table 20a. Chemical analyses of the four sherds, three clay samples and loam from a pit, filled with settlement waste, % of weight.

	WR 75/42	*WR 75/43*	*WR 75/44*	*Wr 75/45*	*B2t*	*C2*	*pit*	*river loam*
SiO_2	60.29	64.87	59.60	74.12	70.59	64.42	68.44	72.48
Al_2O_3	15.75	14.51	16.75	10.52	13.48	9.24	10.69	12.73
Fe_2O_3	5.84	4.87	6.17	4.73	5.40	3.63	4.20	5.02
MnO	0.03	–	0.04	0.01	0.09	0.08	0.12	0.12
MgO	0.79	1.04	1.50	0.82	1.88	1.74	0.99	1.66
CaO	2.22	1.62	2.44	1.15	1.16	5.12	1.50	1.01
Na_2O	0.44	0.03	0.18	0.11	–	–	–	–
K_2O	2.40	1.98	2.27	1.44	2.64	1.92	2.39	2.23
H_2O*	5.09	6.24	4.06	4.05	4.13	11.10	10.53	4.51
TiO_2	0.91	0.79	0.86	0.69	0.75	0.56	0.67	0.87
P_2O_5	6.28	2.32	3.88	1.54	0.16	0.18	0.26	0.27
	100.04	98.27	97.92	99.18	100.28	97.99	99.79	100.90

* loss on ignition

Table 20b. Basic composition.

Cp or P	5.50	2.09	3.92	1.35	0.35	0.42	0.60	0.68
Ru	0.71	0.63	0.67	0.54	0.57	0.47	0.55	0.66
Kp	9.48	8.07	9.06	5.73	10.23	8.25	10.05	8.64
Ne	2.64	0.18	1.08	0.66	–	–	–	–
Cal	7.38	5.55	8.16	3.84	1.58	14.16	4.20	2.07
Sp	3.66	4.95	6.99	3.81	8.52	–	4.86	7.53
Cs	–	–	–	–	–	1.77	–	–
Fo	–	–	–	–	–	4.35	–	–
Fa	–	–	–	–	–	0.12	–	–
Fs	6.86	5.85	7.31	5.55	6.30	4.59	5.37	5.90
C	7.78	8.43	7.08	5.63	6.47	–	4.43	5.93
Q	55.99	64.26	56.24	72.90	65.99	65.33	69.94	68.62

Cp = apatite
Ru = rutile
Kp = kaliophilite
Ne = nepheline
Cal = calciumaluminate
Sp = spinel
Ca = larnite
Fo = forsterite
Fa = fayalite
Fs = ferrisilicate
C = corundum
Q = quartz
P = phosphorus

Table 20c. Ceramic variant of the "norm," valid for 900° C; calculations based on the chemical analysis.

Q	40.29	50.36	38.78	62.87	50.96	51.33	55.23	55.38
Or	15.80	13.45	15.10	9.55	17.05	13.75	16.75	14.40
Plag	9.27	5.38	8.00	7.50	2.63	23.60	7.00	3.00
Mull	14.24	13.45	13.39	7.51	8.63	0.00	7.38	7.91
Cord	6.71	9.08	12.81	6.99	15.62	Fo 4.47	8.91	13.80
Woll	2.90	1.67	2.96	0.00	0.00	2.36	–	–
Hm	4.58	3.90	4.87	3.70	4.20	3.06	3.58	3.93
Ru	0.71	0.63	0.67	0.54	0.57	0.47	0.55	0.66
(Felsp)	(25.07)	(18.83)	(23.10)	(17.05)	(19.68)	(37.35)	(23.75)	(17.40)
P	5.50	2.09	3.42	1.35	Cp 0.35	Cp 0.42	Cp 0.60	Cp. 0.68

Q = quartz
Or = orthoclase
Plag = plagioclase
Mull = mullite
Cord = cordierite
Woll = wollastonite
Hm = hematite
Ru = rutile
(Felsp) = felspars, orthoclase + plagioclase
P = phosphorus
Fo = forsterite
Cp = apatite

calculated quartz content is 62.87% and the lowest is 39.56%. The contents become lower if the somewhat arbitrary wollastonite is left out and calcium aluminate (Cal) is converted entirely into anorthite. To allow comparisons the Cal values have also been included (table 20b). These Cal values show that definitely less calcium felspars can occur in WR 75/45. It is to be noticed that with respect to the measured quartz contents, the data from the X-ray diffraction analysis differ partly from the contents calculated on the basis of the norm. The quartz contents, registered in the arbitrary unit of counts per time unit, are 29, 33, 35 and 40 for WR 75/42, WR 75/43, WR 75/44 and WR 75/45 respectively. The diffractograms confirm that the potsherd WR 75/45 contains significantly less felspar than the other three.

Conspicuous is also the rather constant content of normative mullite in the potsherds WR 75/42, WR 75/43 and WR 75/44, and its low content in WR 75/45. One may assume that the content of normative mullite gives information about the quantity of kaolinite which was originally present in the clay. Apparently the material of which WR 75/45 was made, contained both less felspar and less kaolinite, whereas the content of quartz must have been higher. One wonders whether this conclusion will hold after a correction for the temper, as it is obvious that the contents of felspar and quartz in the potsherd are the result of an addition of the quartz and felspar contents of the clay and of the temper material. However, the results of the microscopic analysis with the point counter indicate that the differences cannot be attributed to the temper material. Another way to study the effect for WR 75/45 is to lower the normative quartz content to the average value of the four potsherds: 48.08. When the sum of the normative phases is then brought back to 100%, the mullite content and the felspar content are still too low in comparison with the values found for the other potsherds. The mullite content then becomes 8.8 and the felspar content 20.0.

RESULTS OF THE X-RAY DIFFRACTION ANALYSIS

After grinding, diffractograms were made of these potsherds with a Guinier de Wolff Camera. The powders were also calcinated at 600° C and at 1000° C and then photographed again. Finally, diffractograms were made of the clay fractions and of the sand fractions of the three earlier mentioned clay samples and of test briquettes fired at circa 1000° C in an oxidizing atmosphere. Diffractograms of the powders of the potsherds and of the clay samples give an insight in the semi-quantitive mineralogical composition of the potsherds and of the clay. In the untreated potsherd samples, the mineral quartz, plagioclase, microcline, wollastonite and diopside are found besides the illuviated illite.

Conspicuous is the absence of both hematite and spinel (which originates by burning kaolin). Also mullite, cordierite and magnesium-containing phase were not found. Because of the high phosphorus content, a thorough search was made for possible phosphates. Crystalline phosphates are apparently absent in the analyzed potsherds. Finally, the large quantity of calcium suggests the presence of gehlenite, which was not found.

After calcination, the potsherd samples no longer show lines of micas, or illite. But mica is clearly visible in the thin sections, so that it might be expected that at this low temperature the mica which has come with the coarse sandy temper, would still be visible. Since this is not the case, it can be suggested that because of the termal treatment in the past and the subsequent chemical influence of the soil development, the still-visible mica has lowered heat-resistance. Muscovite does not normally disintegrate until 800 to 900° C.

The diffraction pattern contains no crystalline iron minerals such as goethite, magnetite or hematite. Also heating to 600° C does not let these phases develop, although goethite, when present in the amorphous state (in which it is, as appears from the microscopic analysis), converts into hematite at circa 330° C. Only after heating to 1000° C do lines of hematite occur in the pattern. Weak lines of hematite occur in the test briquettes fired of clay.

The above indicates that the pottery must have originated in a partially reducing environment at temperatures higher than circa 550° C but lower than circa 900° C, the temperatures at which gehlenite and cordierite develop. The absence of hematite and crystalline goethite does not necessarily point to low temperatures, because the hematite, which was present in the test briquettes and which developed at high temperatures, can very well have been reconverted into non crystalline goethite because of its long stay in the soil.

The results regarding the quartz and felspar contents have been given already on p. 197.

The X-ray diffraction analysis of the B2t and the C2 of the loess, and of the river loam, shows that both loess samples are characterized by a relatively high kaolinite content besides considerable amounts of montmorillonite and illite. The river loam has less clay fraction than the other samples, but the composition of the clay fraction is not different from the rest. A table of the peak areas shows the shares of the three clay minerals in the three samples (table 21). No quantitative ratio of the clay minerals should be concluded from these peak areas. They only give an indication of the relative increase and decrease.

Table 21. Relative ratio of the peak areas of the clay fraction of the three clay samples.

	Kaolinite	*Illite*	*Montmorillonite*
C2	14	10	76
B2t	8	16	76
river loam	12	14	74

A diffractogram of the fraction larger than 50 μm of the clay samples shows that they contain almost no felspar. Many felspars are found, however, in the fraction smaller than 50 μm of the loess. These felspars are the same as those found in the potsherd powders. The felspar assemblage of the river loam is clearly different.

RESULTS OF THE THERMAL ANALYSIS

TG and DTA analyses were made of the ground potsherd samples. The results are given in figure 35 and figure 36. The TG analyses show that the heating to 1000° C causes the following losses of weight:

WR 75/42 – 9.6%, WR 75/43 – 6.8%, WR 75/44 – 4.5% and WR 75/45 – 4.7%. At a heating of 20°/min, the loss of weight has disappeared at circa 500° C. Part of the loss of weight must be attributed to the loss of the water which the potsherd has absorbed in the soil in the course of time, some of which is rather firmly bound. Further, the dehydration of the illuviated clay minerals and of the possible present amorphous goethite plays a part. The disappearance of carbon must also be taken into account.

The DTA analysis shows a loss of moisture between 100° C and 170° C, followed by a more or less pronounced exothermic reaction. Especially WR 75/43, a thoroughly dark-coloured, almost black potsherd, shows this exothermic reaction very pronouncedly. The reaction is attributed to the disappearance of carbon. WR 75/43 must have been a sample rich in carbon. The carbon-content and thus the black colour can have been caused by the smothering of the pottery. It is known that pottery which is

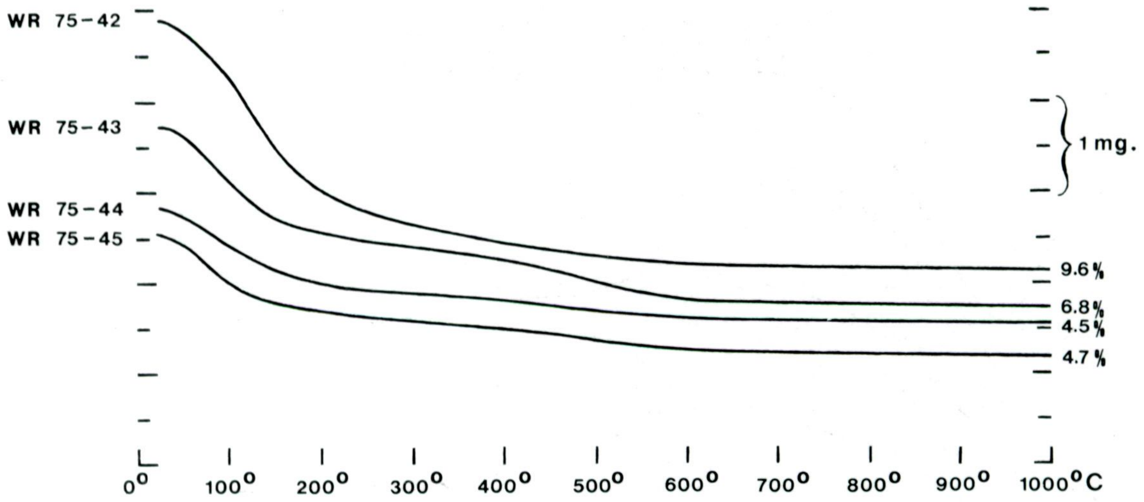

Fig. 35. Results of the TG analysis of four LBK sherds from Hienheim.

reduced at a lower temperature, e.g. in hay or saw-dust, immediately turns thoroughly black because of the reduction of the iron to FeO, wüstite, and as a result of absorption of carbon by the potsherd. This carbon can be removed again by burning.

Reactions of clay minerals or carbonate have not been found in the thermal analyses and are not to be expected either, in view of the results of the X-ray analysis.

An X-ray diffractogram at rising temperature was taken of one sample, WR 75/42. The result of this analysis provided no new information, so that this method has been left out, for the time being, for the other samples.

DISCUSSION AND REMARKS

On the basis of the mentioned methods, the question which materials were used for making the four LBK potsherds can be answered partly. The white loam from the Hienheimer Forst does not qualify because of its poor firing behaviour. It is rather certain that the calcareous C2 loess was not used either. The Ca content of this material is too high and besides, the ceramic product made of the C2 loess is of poor quality. The analyzed river loam contains other felspars than those found in the potsherds, and perhaps it also has a too small clay fraction to be the raw material. The B2t loess has the best qualities. The felspar content of this loam corresponds in many respects to that of the potsherds. However, the clay which was used, must have been slightly more calcareous than the present B2t. As we do not know yet which treatment the occupants of the excavated settlement used to make their clay suitable for the manufacture of pottery, it cannot be said with absolute certainty that the local loess was used. What is certain is, that the loess must have undergone a special treatment to reach the composition as found in the sherds. This can be concluded from the high P_2O_5 content of the potsherds. A temper with bone was thought of in the first place.

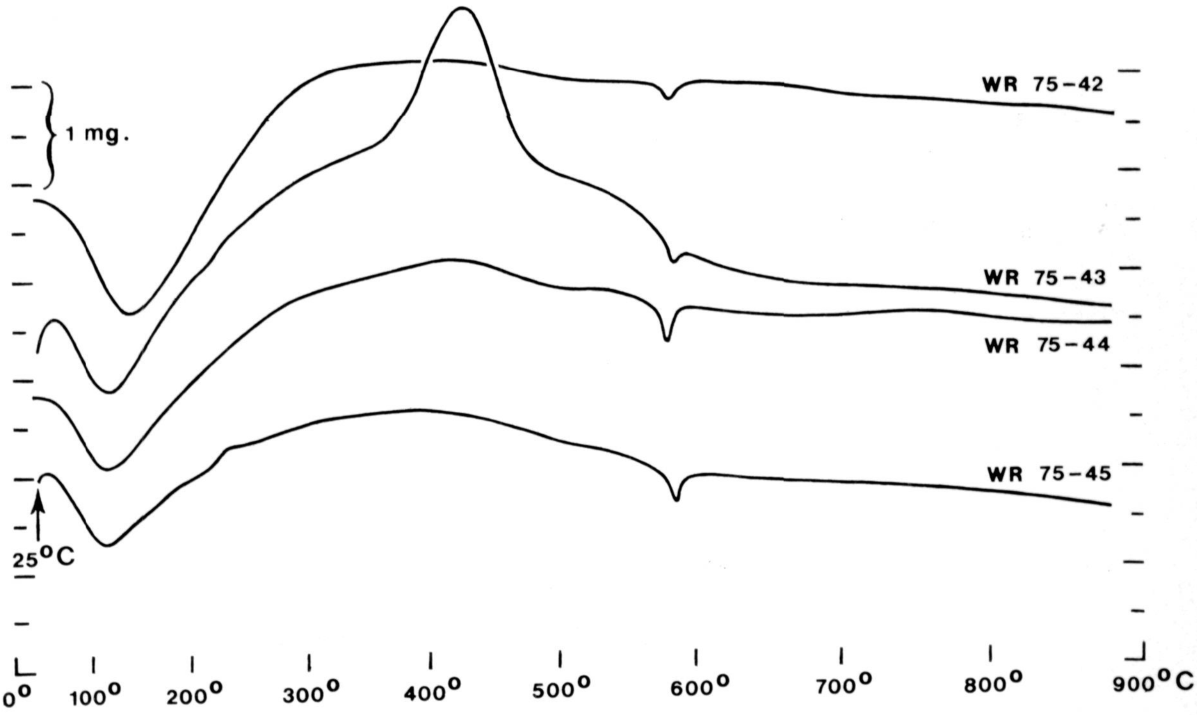

Fig. 36. Results of the DTA analysis of four LBK sherds from Hienheim.

If a temper with bone is assumed to explain the high phosphorus content and if $Ca_{10}(PO_4)_6(OH)_2$ is taken as average bone composition, then one introduces 10 calcium ions with each 6 phosphorus ions, or, to stay within the terms of the calculation, each cation per cent phosphorus means 1.7 cation per cent calcium. This subsequently means 5.1% Cal. and finally 8.5% calcium felspar or anorthite and the necessary decrease of the calculated quartz content and demonstrates that a B2t loess with a temper additive of ground bone must have received a considerable enrichment in calcium. That calcium content is amply sufficient to explain the difference in calcium content between the present B2t and the found potsherds. In general, it can even be said that the calcium contents of the potsherds are too low to assume that the high phosphorus content can be attributed exclusively to the addition of fresh bone meal. In this connection, it must be noticed that it is possible that a part of the lime was converted into CaO and subsequently dissolved when the pots were used. It is conspicuous, however, that the pots were not cracked by the hydrolysis of this CaO.

Finally it is also possible that calcinated bones were used as temper material. Calcination followed by leaching with water, before the material is added to the clay, can lead to an enrichment in phosphorus without all calcium contained originally in the bones ending up in the pottery.

The results also provide some information about the firing process. The potsherds must have developed in a reducing environment at temperatures between 550° C and 900° C. Such an environment can be created with a fire which is laid in a hole in the ground and covered later with straw or sods. A test-firing of pots, made according to this method with loess from Hienheim, showed that the pottery made in this way was not very different from the excavated potsherds.

As the examination was restricted to four potsherds from one single pit, the conclusion should not be drawn that these results are generally valid. It is necessary to submit large numbers of potsherds from as many pits as possible to a comparable examination. This work has been started in the meantime. Moreover it is desirable to carry out certain firing tests.