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Dedicated to Professor Lisa Heller-Kallai on the occasion of her 65^{th} birthday

THE FIRING TEMPERATURE OF A PERSIAN-PERIOD POTTERY KILN AT TEL MICHAL, ISRAEL, ESTIMATED FROM THE COMPOSITION OF ITS POTTERY

S. Shoval

Geology Group, The Open University of Israel, 16 Klausner St., Tel Aviv and the Geological Survey of Israel, Jerusalem

Abstract

The firing temperature of a Persian-period kiln excavated at Tel Michal (Makmish), on the Mediterranean coast north of Tel Aviv, Israel, is estimated from the composition of its pottery, using X-ray diffraction and IR spectroscopy methods. The kiln was built with two chambers: an upper one where the vessels were fired and a lower one for the burning. Storage jars that had been fired and remained inside the kiln are composed of lime tempers and quartz sand in a fired clay matrix that contains amorphous material and the high-temperature Ca-silicates gehlenite and anorthite. The tempers are composed of re-formed calcite. Thermal simulation indicates that the composition is compatible with a heating temperature of 800–900°C, which represents the firing temperature in the upper chamber of the kiln.

Keywords: firing temperature, IR spectroscopy, pottery kiln, re-formed calcite

Introduction

A collapsed Persian-period (5th–4th centuries B. C. E.) pottery kiln was excavated in Tel Michal (Makmish), on the Mediterranean coast north of Tel Aviv [1, 2]. The kiln was apparently a dome-shaped structure and consisted of two chambers, separated by a horizontal partition. The upper chamber of the kiln was used for firing the pottery and the lower one for burning. Five storage jars of the same type and fabric were found inside it and reconstructed [1, 2]. The structure of the kiln, the raw materials used for building it and the burning temperature in the lower chamber of the kiln, as estimated from the composition of slag-like material formed in its wall, are demonstrated in a separate paper [3].

During firing of raw materials to pottery, processes of dehydroxylation of clay minerals, as well as formation of X-ray amorphous material, usually occur

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[4, 5]. After firing, some clay minerals in the fired matter may rehydroxylate and reconstruct [6–8]. During firing of calcareous raw material, processes of decarbonation of the calcite usually occur [4]. At higher temperatures Ca-silicates, namely gehlenite [$Ca_2Al_2SiO_7$], plagioclase-anorthite [$CaAl_2Si_2O_8$] and pyroxene-diopside [$CaMg(SiO_3)_2$], are formed due to the thermal reaction of the calcite decomposition products with the fired clay [5]. After firing, re-formed calcite may be recarbonated from the remaining decarbonation products of the original calcite that did not react with the clay during firing [9].

The composition of the pottery depends on the temperature of the firing [10–13]. The common method used for estimation of the firing temperature is X-ray diffraction, based on determination of the mineral assemblage formed in the fired matter due to the destruction of original minerals and the crystallization of new minerals. However, this method is limited to examination of crystallized materials. On the other hand, IR spectroscopy enables identification of the changes in the amorphous fired clay as a function of the firing temperature [14].

The purpose of this study was to estimate the firing temperature of the pottery in the upper chamber of the Tel Michal kiln by these different methods. Thermal simulation was made on the same raw material as that used for the pottery. The study established the link between the firing temperature and the type of ancient kiln in which the temperature was obtained.

Experimental

Samples

Samples from the storage jars found inside the kiln and local raw materials were examined. The pottery was excavated in the framework of the 'Tel Michal Archaeological Project' [1, 2].

Methods

The samples were investigated by the following methods. Petrographic analyses were made by examining thin sections of the samples under a polarizing microscope. X-ray powder diffractions were made using a Philips PW-1820/00 diffractometer with Cu-irradiation. IR spectra were recorded in KBr disks using a Nicolet ZDX FT-IR spectrometer. Disks were prepared using 1 or 5 mg of the sample and 150 mg of KBr. The disks were dried for 24 h at 110 and at 300°C for the investigation of SiO and OH regions of the spectra, respectively. The higher temperature is needed to remove stable water bands which mask the OH stretching band [6]. Immediately after heating, the dried disks were re-pressed (without re-grinding) in order to improve the resolution of the spectra.

Results

The Pottery Matter

In order to estimate the firing temperature of the pottery in the upper chamber of the kiln, the composition of the storage jars fired in it was determined. All the investigated jars from the kiln gave similar results:

- The petrographic analyses show that the pottery is composed of sub-rounded to rounded medium-size quartz sand and lime tempers in a fired clay matrix.
- A representative X-ray diffractogram of the pottery is demonstrated in Fig. 1a. The samples contain mostly quartz, calcite and the high-temperature Ca-silicates gehlenite and plagioclase-anorthite. Hematite is also present.
- A representative IR spectrum of the pottery is shown in Fig. 2a. The bands are assigned according to their locations [15, 16]. The SiO stretching band splits to 1053 and 1078 cm^{-1}, which are connected with the fired clay. The SiO deformation band appears at 462 cm^{-1}. OH stretching band is absent. The main CO_3 band region in the IR spectrum of the pottery is shown in Fig. 3a. This band is related to calcite and is characterized by a broad top and a shift to 1445 cm^{-1}, compared to that of the unheated limestone tempers (Fig. 3b).

Thermal analysis

In order to determine the temperature which was needed to form compositions similar to those of the pottery, thermal simulations were made. A local sandy clay raw material (Hamra soil) [3], which has petrographic features similar to that of the pottery, was heated in an electric kiln to temperatures between 600–1000°C for various durations. After heating, the fired raw materials were rehydrated and recarbonated, using returning soaking and drying in the open air for some months.

X-ray diffractograms of the sandy clay raw material, which includes limestone tempers, before heating and after heating for 6 hours at 800–900°C, are shown in Fig. 1b–d. The changes in mineral assemblage, dependent on the heating temperatures, are:

- The unheated raw material contains clay minerals, quartz and small amounts of plagioclase potassium, feldspar and hematite. In oriented samples the clay minerals kaolinite, montmorillonite and some illite are identified. The limestone tempers are composed of calcite.

– After 800°C most of the clay minerals were decomposed. Calcite is present (after the recarbonation).

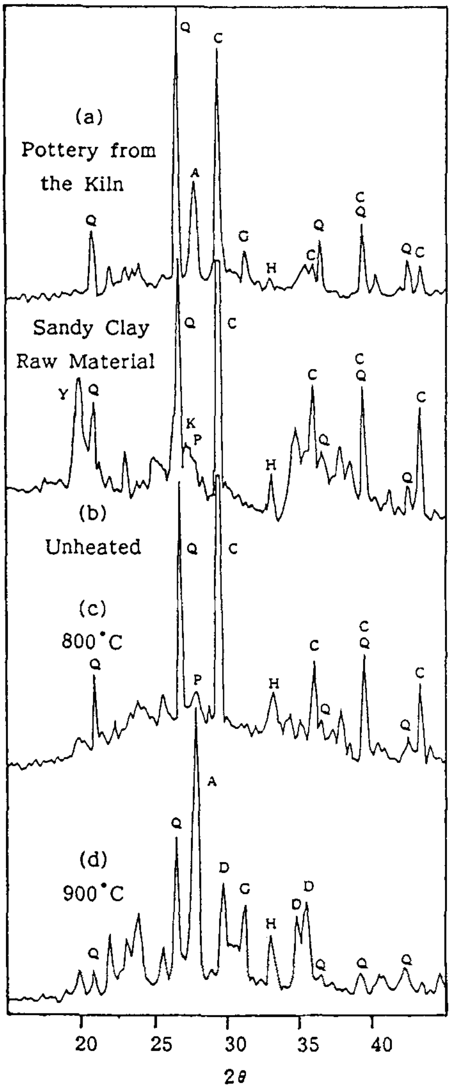

Fig. 1 X-ray diffractograms (Cu-irradiation) of: (a) pottery from the kiln; (b) unheated sandy clay raw material which includes limestone tempers; (c,d) the same raw material after 6 h of heating at 800 and 900°C, respectively. After heating, the fired raw materials were rehydrated and recarbonated (Y = clay minerals, C = calcite, Q = quartz, P = plagioclase, K = potassium feldspar, G = gehlenite, A = anorthite, D = diopside and H = hematite)

– After 900°C high-temperature Ca-silicates are observed: gehlenite, a noticeable amount of plagioclase-anorthite and pyroxene-diopside. Hematite is also present. Calcite is not observed.

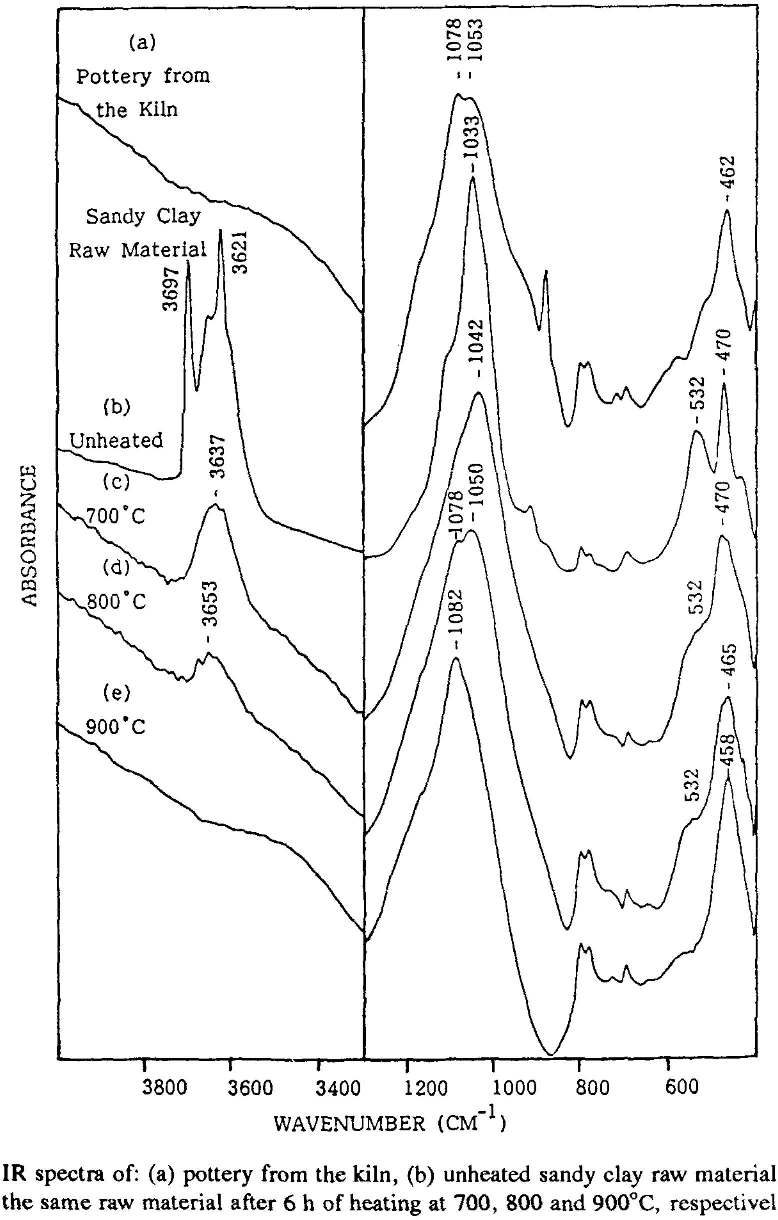

Fig. 2 IR spectra of: (a) pottery from the kiln, (b) unheated sandy clay raw material; (c–e) the same raw material after 6 h of heating at 700, 800 and 900°C, respectively. After heating the fired raw materials were rehydrated and recarbonated. The disks were dried at 110 and at 300°C for the investigation of SiO and OH regions of the spectra, respectively

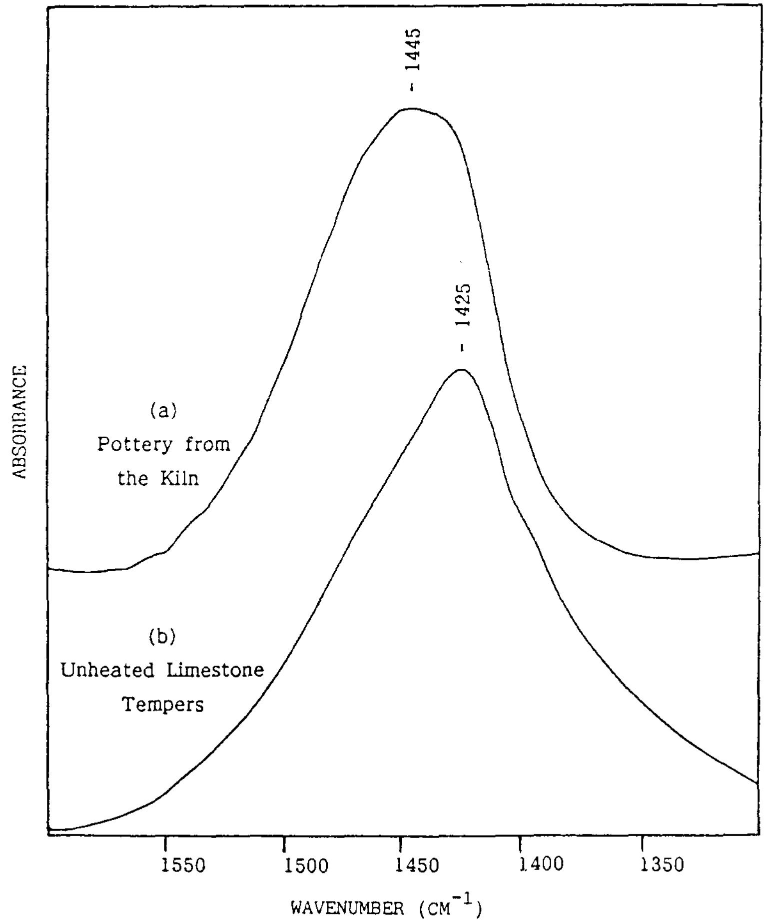

Fig. 3 IR spectra of the main CO_3 band in: (a) pottery from the kiln; (b) unheated limestone

IR spectra of the sandy clay raw material before and after heating for 6 hours at 700–900°C are shown in Fig. 2b–e. The changes in the spectra, dependent on the heating temperatures, are:

– In the unheated raw material the SiO stretching band appears at 1033 cm^{-1}, which characterizes clay. The SiO deformation band appears at 470 cm^{-1}. The strong OH stretching bands of kaolinite appear at 3621 and 3697 cm^{-1}. The band at 3621 cm^{-1} overlaps those of montmorillonite and illite. The deformation band connected with the AlO vibration appears at 532 cm^{-1} and it is relatively strong.

– After 700°C the SiO stretching band is broader and shifts to 1042 cm^{-1}. The OH stretching bands degenerated to one weak band at 3637 cm^{-1}. The deformation band connected with AlO vibration is transformed to a shoulder.

– After 800°C the SiO stretching band split to 1050 and 1078 cm^{-1}. The SiO deformation band shifts to 465 cm^{-1}. The OH stretching band is very weak at 3653 cm^{-1}.

– After 900°C the SiO stretching band appears at 1082 cm^{-1} without splitting. The SiO deformation band shifts to 458 cm^{-1}. The OH stretching band and the deformation band connected with AlO vibration are absent.

Discussion

The Tel Michal kiln undoubtedly collapsed at the end of the last firing and was then abandoned [2]. The storage jars investigated were found inside the kiln and were surely fired in it. Petrographic analyses show that sandy clay was the raw material used for the jars found inside the Tel Michal kiln. This raw material was probably local and taken from a sandy clay soil (Hamra soil) near the site or from a nearby stream alluvium (Nahal Gelilot). Both the sandy clay and the pottery material contain sub-rounded to rounded medium-size quartz grains in clay or in a fired clay matrix, respectively. The lime tempers in the pottery probably have another source.

Thermal simulation

The firing temperature of the pottery in the upper chamber of the kiln can be estimated by thermal simulation and comparison of the composition of the pottery with that of the sandy clay raw material heated at known temperatures. The results from heating this raw material to temperatures between 700–900°C for 6 hours are presented. This heating time is reasonable for pottery firing and completion of the indicative thermal reactions at each temperature. In accordance with the processes which take place in the pottery after firing, those heated raw materials were rehydrated and recarbonated before examination.

X-ray diffraction

Thermal simulation shows that the high-temperature Ca-silicates, gehlenite, plagioclase-anorthite and pyroxene-diopside, are first observed in the raw material, which contains limestone tempers, after heating to 900°C (Fig. 1d). Those minerals were not detected in the raw material heated to 800°C, indicating that they start to form between those temperatures. The appearance of these high-temperature Ca-silicates was observed at 850°C [10], their amount increasing with rising temperatures. The increased content of plagioclase-anorthite is related to the reaction of gehlenite with SiO_2 at higher temperatures [10]. After 800°C the calcite is re-formed, since the original limestone tempers were totally decomposed at this temperature [9]. Re-formed calcite is not observed after 900°C due to the total thermal reaction of its decomposition products with the fired clay.

Presence of gehlenite and anorthite in the pottery (Fig. 1a) indicates that the firing temperature was above 800°C. On the other hand, a large amount of calcite, the absence of diopside and the low amount of anorthite in the pottery indicate firing below 900°C. According to this firing temperature it seems that the calcite in the pottery is re-formed.

IR spectroscopy

The IR spectrum of the pottery shows that the bands of the fired clay are dominant. The bands characterizing high-temperature Ca-silicates are practically not observed in the spectrum, indicating their low degree of crystallinity and their distortion by the dominant overlapping bands of the amorphous fired clay. The comparison between the IR spectrum of the pottery and the spectra of the heated raw material takes into consideration the presence and the strength of the OH bands, and the locations and widths of the SiO bands which are functions of the destruction of clay minerals and crystallization of new minerals. The width and the location of CO_3 bands in connection with original or re-formed calcite depend on the firing temperature.

– OH bands

The OH stretching band is usually distorted by the overlapping bands of stable water which are absorbed by the amorphous fired clay. Therefore, drying the disks at about 300°C for 24 h is needed for their observation [6]. Thermal simulation shows that the presence and strength of the OH stretching band in the IR spectra of the heated raw material are functions of the firing temperature. After the rehydration of the heated raw materials the OH stretching band decreases progressively with increasing temperatures. Only a weak OH stretching band appears at 3653 cm^{-1} in the raw material heated to 800°C, which is absent at 900°C (Fig. 2d,e). The decrease is due to the progressive dehydroxylation of the clay minerals during the heating. After heating up to about 800°C, partial rehydroxylation and reconstruction occur [8]. Above this temperature nonreversible dehydroxylation of the clay minerals takes place [6]. The OH stretching band is absent in the pottery (Fig. 2a) indicating that the firing temperature was above 800°C.

In the IR spectrum of montmorillonite the band at 522 cm^{-1} is assigned to SiOAl deformation [16], while in kaolinite the band at 540 cm^{-1} is assigned to AlO deformation [17]. In the unheated raw material this band appears at

532 cm^{-1} and decreases progressively with increasing temperatures. Thermal simulation shows that this band is transformed to a weak shoulder in the raw material heated to 800°C and disappears at 900°C (Fig. 2d,e). Since at increasing temperatures the intensity of this band decreases, in accordance with the intensity of the OH stretching vibration, its seems that it is also connected with the OH-group. It is suggested that this band is connected with an OH librational mode. The pottery shows only a weak shoulder in the range of this band (Fig. 2a), indicating that the firing temperature was above 800°C. Its existence indicates that the temperature was below 900°C.

– SiO bands

The location and the width of the SiO stretching band in the IR spectra of the heated raw material are functions of the firing temperature. Thermal simulation shows that this band broadened and progressively shifted from 1033 cm^{-1} in the unheated raw material to higher frequencies: 1042 cm^{-1} at 700°C and doublet at 1050 and 1078 cm^{-1} at 800°C (Fig. 2c,d). The SiO stretching band appears at 1082 cm^{-1} in the raw material heated to 900°C (Fig. 2e). The shifting is connected with progressive destruction of the clay minerals in the fired matter, formation of amorphous material, and crystallization of new minerals at elevated temperatures. The location and splitting of the SiO stretching band in the pottery at 1053 and 1078 cm^{-1} (Fig. 2a), is compatible with that of the raw material heated to 800°C, indicating that pottery was fired at about this temperature. The progressive changes in the SiO stretching band in the IR spectrum of raw material heated to 900°C indicated a lower firing temperature.

The SiO deformation band also progressively shifted with increasing temperatures. Thermal simulation shows that this band shifted to lower frequencies, from 470 cm^{-1} in the unheated raw material to 465 and 458 cm^{-1} in the raw material heated to 800 and 900°C, respectively (Fig. 2d,e). The location of the SiO deformation band in the pottery at 462 cm^{-1} (Fig. 2a) indicates that the pottery was fired between these temperatures.

– CO_3 bands

The main CO_3 band in the IR spectrum of unheated limestone tempers is characterized by a relatively sharp top and location at about 1425 cm^{-1} (Fig. 3b). On the other hand, this band in pottery and in ancient calcareous cements containing re-formed calcite is characterized by a broad top and a shift to higher frequencies [18]. The broadening is due to the low degree of crystallinity of the recarbonated calcite [9] and the shifting is probably connected with impurities of iron and magnesium, which resulted from re-formation of the calcite in the fired clay matrix. Limestone tempers are almost totally decarbonated in raw material heated to about 700°C [9].

According to the broadness at the top of the CO_3 main band and the shift to 1445 cm^{-1} in the IR spectrum of the pottery investigated (Fig. 3a), it is assumed that the original calcite was decomposed and that it was re-formed, indicating a firing temperature above 700°C. The high intensity of this band in the pottery indicates that the firing was below 900°C, since re-formed calcite is absent above this temperature due to total reaction with the fired clay.

Conclusions

The X-ray diffraction and IR spectroscopy results are in agreement with a heating temperature of 800–900°C, which represents the firing temperature in the upper chamber of the Tel Michal kiln. The thermal simulation results that were taken into consideration are those of raw material heated for 6 hours, which is reasonable for pottery firing and completion of the indicative thermal reactions, at each temperature. The IR spectrum of the pottery is compatible with that of the raw material heated between those temperatures and differs from that of the unheated raw material:

- The OH stretching band is absent, due to total nonreversible dehydroxylation of the clay minerals in the firing. The band, which is probably connected with an OH librational mode, is transformed to a weak shoulder.
- The SiO stretching band shifts to higher frequencies, splits and broadens due to destruction of the clay minerals in the fired matter, formation of amorphous material and crystallization of new minerals. The SiO deformation band is shifted to lower frequencies.

The main CO_3 band in the IR spectrum of the pottery differs from that of the unheated limestone tempers. Its broadening and shifting to higher frequencies characterize re-formed calcite, which has a low degree of crystallinity and probably contains impurities of iron and magnesium.

In order to obtain this firing temperature of the pottery in the upper chamber of the kiln, a higher burning temperature was needed in its lower chamber [3], due to the thermal gradient and the presence of a horizontal partition separating those two chambers, on which the vessels were placed for firing.

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References

1 Z. Herzog, O. Negbi and S. Moshkovitz, 'Excavation at Tel Michal', Institute of Archaeology, Tel Aviv University 1978, p. 119.
2 Z. Herzog, G. Rapp, and O. Negbi 'Excavation at Tel Michal, Israel', Institute of Archeology, Tel Aviv University 1989, p. 102.
3 S. Shoval, J. Thermal Anal., 39 (1993) 1157.
4 R. C. Mackenzie, 'Differential Thermal Analysis', Academic Press, London 1970, 1972.
5 S. Shoval, Thermochim. Acta, 135 (1988) 243.
6. S. Shoval, P. Beck, Y. Kirsh, D. Levy, M. Gaft and E. Yadin, J. Thermal Anal., 37 (1991) 1579.
7 R. E. Grim and W. F. Bradley, Amer. Min., 33 (1948) 50.
8 L. Heller, V. C. Farmer, R. C. Mackenzie, B. D. Mitchell and H. F. W. Taylor, Clay Minerals Bull., 5 (1962) 56.
9 S. Shoval, M. Gaft, P. Beck and Y. Kirsh, J. Thermal Anal., 40 (1993) 263.
10 M. Maggetti, British Museum Occasional Paper, 19 (1981) 33.
11 W. D. Kingery and J. D. Friedman, Proc. Prehistoric Soc., 40 (1974) 204.
12 M. Maggetti, H. Westley and J. S. Olin, in 'Archeological Chemistry', Am. Chem. Soc. (1984) 151–191.
13 Y. Maniatis and M. S. Tites, J. Arch. Sci., 8 (1981) 59.
14 S. Shoval, Abstract, Israel Geological Society Annual Meeting Proceedings, 1993, p. 119.
15 V. C. Farmer, 'The Infrared Spectra of Minerals', Mineralogical Society, London 1974, p. 331.
16 H. W. van der Marel and H. Beutelspacher, 'Atlas of Infrared Spectroscopy of Clay Minerals and their Admixtures', Elsevier, Amsterdam 1976, p. 57.
17 S. Yariv, Intern. J. Trop. Agri., IV (1986) 310.
18 S. Shoval and N. Goldman, Abstract, Israel Geological Society Annual Meeting Proceedings, 1993, p. 125.

Zusammenfassung — Mit Hilfe von Röntgendiffraktion und IR-spektroskopischen Methoden wurde die Brenntemperatur eines bei Tel Michal (Makmish), an der Mittelmeerküste nördlich von Tel Aviv ausgegrabenen Töpferbrennofens aus der Perserzeit anhand der Zusammensetzung der Töpferwaren geschätzt. Der Brennofen wurde mit zwei Kammern gebaut: eine untere für den Heizvorgang und eine obere, in der die Gefäße gebrannt wurden. Im Ofen gebrannte und dort verbliebene Vorratsgefäße, gebildet aus Kalkgemisch und Quarzsand in einer gebrannten Tonmatrix, welche amorphes Material sowie die Hochtemperatur-Calciumsilikate Gehlenit und Anorthit enthält. Die Gemische bestehen aus umgewandeltem Kalzit. Eine thermische Simulation zeigt, daß deren Zusammensetzung mit einer Heiztemperatur von zwischen 800 und 900°C entspricht, was die Brenntemperatur der oberen Ofenkammer darstellt.